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From antiquity to the early nineteenth century

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Author of *The Scientific Work of René Descartes* (1596–1650), *Mathematical Work of John Wallis, D.D., F.R.S.* (1616–1703), and other works

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On the Theory of Cooperative Phenomena in Crystals

By C. Domb
King's College, Strand, W.C.2

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§ 1. INTRODUCTION

1.1. *Cooperative Assemblies*

THE physical phenomena to which statistical mechanics has been applied can, broadly speaking, be divided into two categories. In the first category the microscopic systems of which the statistical assembly is composed can be regarded to a good approximation as non-interacting. The fundamental results of statistical mechanics relate thermodynamic functions to the energy levels of the total assembly, and the latter can be determined quite simply from the energy levels of the individual microscopic systems. If the systems obey Bose–Einstein or Fermi–Dirac statistics an elementary combinatorial problem must be solved, but this involves no serious difficulty. Of course there must be sufficient interaction between the systems for equilibrium to be reached during the time considered, and for statistical mechanics to be applicable; but we can reasonably assume that equilibrium can be achieved by interactions which make a negligible direct contribution to the energy levels of the assembly.

Examples of phenomena of this kind are the specific heats of gases, and solids, chemical reactions in gases and their equilibrium constants, the energy distribution of black-body radiation, paramagnetism, the elementary electron theory of metals, and the condensation of a perfect Bose–Einstein gas. In the case of solids, although the interactions between individual atoms or molecules play an essential part, their departures from equilibrium are quite small over a substantial temperature range. Hence, by a transformation to normal coordinates the solid can be treated as an assembly of non-interacting harmonic oscillators. With the exception of the Bose–Einstein condensation, the thermodynamic properties of assemblies of the first category are smooth and continuous, and the results obtained by the application of statistical mechanics to these assemblies can be considered as most satisfactory.

In regard to assemblies of the second category, however, the situation is very different. For the most part the physical phenomena which they attempt to account for contain discontinuities corresponding to phase transitions of various kinds. Examples are the condensation of gases, the melting of solids, the properties of the liquid state (including the phenomena associated with the critical point), the properties of solutions and the conditions for phase separation, the form of solubility curves, various types of λ-point transition (order disorder transitions, the liquid helium transition, the superconducting transition), and ferromagnetism. For assemblies of this kind the interactions between individual microscopic systems play an essential part, and cannot be removed by elementary transformations.

The energy levels of the assembly are not simply related to those of the microscopic systems, and the interactions cause the cooperation of large numbers of systems giving rise to phenomena such as those listed above. The terms 'cooperative phenomena' and 'cooperative assemblies' are therefore often used to describe the second category. The exceptional case of a Bose–Einstein condensation referred to above in the first category can also be considered as arising from an attractive interaction between the particles, Bose–Einstein statistics being equivalent to such an attraction.

1.2. *Simplified Models and Approximations*

The mathematical problems associated with cooperative assemblies are extremely formidable. To facilitate calculations models have been introduced in which the molecular interaction is simplified, but which, it is hoped, maintain the cooperative characteristics of the original assembly; examples are the use of hard sphere molecules in elucidating the properties of liquids, and the neglect of all but nearest neighbour interactions in problems on crystal lattices.

For the most part even the simplified problems still show little hope of exact solution, and approximations have been introduced (e.g. the superposition approximation in the theory of liquids Kirkwood 1935, Kirkwood *et al.* 1950, Born and Green 1946, 1949). To make effective use of such approximations it is very desirable to have some means of estimating the error involved, and hence of delineating the region in which the approximation is reliable. It has become fairly clear that in the critical region of phase transitions single approximations are unreliable, and the only hope of deriving information is by assessing the trend of a series of successive approximations; but for the theory of liquids even the simple approximations involve intricate and complex calculations, and there have been few attempts at higher order approximations. Recently numerical computations on an assembly of hard spheres (Alder and Wainwright 1957, Wood and Jacobson 1957) have given very strong indications of a first-order phase transition at a definite specific volume; no such firm conclusion could be drawn from approximate treatments.

In regard to cooperative phenomena in crystals the situation is appreciably better. A particular set of exact solutions exists for two-dimensional models. These exact solutions are most valuable, and demonstrate clearly that even the simplest type of interaction causes the nature of the solution to change completely, and gives rise to characteristic singularities in the thermodynamic functions of the assembly. For three-dimensional models, although exact solutions still seem far off, approximate methods and series expansions have been developed to quite a high order in recent years. It now seems possible to specify with confidence many of the important thermodynamic properties of simple models, and hence, if there is disagreement with experimental results, this must be due to the nadequacy of the model and not to a particular approximation.

1.3. *Scope of the Present Article*

The present article is concerned with cooperative phenomena in crystals. In § 2 the general theory of regular assemblies is developed, and the basic mathematical problem which they pose is formulated. The relationship oi various simplified physical models to this problem is established. § 3 attempts to give an account of the exact information which is available. The main emphasis is on the physical conclusions, but some effort has also been made to summarize the important mathematical methods. § 4 deals with approximate methods, particular consideration being paid to the systematic development of successive approximations. By carefully examining the trends of these approximations an assessment is made of the physical properties of three-dimensional models. The approximations considered in § 4 include the use of finite numbers of terms of exact series expansions, and technical problems connected with the evaluation of terms of such expansions are dealt with in § 5. These terms can be related to the topological properties of finite configurations on crystal lattices, and special methods have been devised in recent years of determining these properties. The results of § 5 are also of relevance to a detailed discussion of ferromagnetism and antiferromagnetism on the Ising and Heisenberg models which the writer hopes to include in a subsequent publication. The choice of material for § 4 has of necessity been somewhat arbitrary. The general criterion has been to include properties of general significance to the theory of phase transitions, and to defer properties which are more specifically magnetic (e.g. the magnetic susceptibility at temperatures above the Curie point) to the subsequent publication. The latter will also contain some exact results of relevance to magnetism which have been obtained recently, and will endeavour to provide a summary of other cooperative problems on crystal lattices which are not dealt with in the current text.

The literature on cooperative phenomena in crystals is very extensive and no attempt has been made to give adequate reference to all research work on the subject. The main reason for writing the article was the feeling that a stage had now been reached at which definite conclusions could be drawn regarding the behaviour of simple models of such cooperative phenomena. The article attempts to explain the major developments leading to such conclusions.

The question of suitable notation has been a continual source of difficulty because of the many different symbols which had to be used. A list of the principal symbols in order of their introduction is therefore provided. As far as possible the individual chapters are self-contained.

Throughout the preparation of the article the writer has drawn freely on the help of his colleagues Dr. M. E. Fisher and Dr. M. F. Sykes, and his former research student Dr. J. M. Burley; all of these placed at his disposal the results of their investigations before publication. More specifically he is indebted to Dr. M. E. Fisher for a careful and critical examination of § 3, to Dr. D. M. Burley for advice in connection with § 4, and to Dr. M. F. Sykes for collaborating in the writing of § 5. Work on the article began during the tenure of a visiting professorship at the University of Maryland; the facilities granted by this University are also gratefully acknowledged.

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§ 2. REGULAR ASSEMBLIES

2.1. *Introduction*

For many of the cooperative assemblies mentioned in § 1 a classical approximation is adequate, and we can consider our molecular constituents as point particles with an interaction energy between any pair which depends on their distance apart. The total energy of the assembly is then the sum of all such possible binary contributions. Clearly the properties of the assembly are determined by the form of the intermolecular potential energy, and we should have to take account of all possible distances of interaction. However, the problem is simplified if the molecules are situated on a crystal lattice, since only values of the interaction at a discrete series of points need be considered. If further we make the assumption that the intermolecular forces are of sufficiently short range for all but nearest neighbour interactions to be neglected, we need consider the value of the interaction energy at one point only. This provides us with the simplest possible model of a cooperative assembly to which the term 'regular assembly' has been assigned by Fowler and Guggenheim (1939).

A regular assembly thus possesses the following properties:

(1) Any configuration of the assembly can be described by specifying the number and geometry of occupiable sites in the assembly and how each site is occupied.

(2) Interactions between pairs of molecules that are not nearest neighbours may be neglected, and therefore the interaction energy of the systems composing the assembly can for each configuration be expressed as the sum of contributions from each pair of immediate neighbours.

Because of their simplicity a great deal of attention has been devoted to the study of regular assemblies.

Let us first consider a regular assembly consisting of a mixture of two types of system which we label 1 and 2. Let N_1 be the number of systems of type 1, N_2 the number of type 2, the total number of lattice points being N $(=N_1+N_2)$.

When the systems are arranged in some configuration on the lattice, the energy will be determined by nearest neighbour interactions, and let N_{11}, N_{12}, N_{22} denote the number of 1–1, 1–2 and 2–2 pairs in this configuration; let ϵ_{11}, ϵ_{12}, ϵ_{22} denote the corresponding interaction energies. Then the energy of this configuration is

$$N_{11}\epsilon_{11}+N_{12}\epsilon_{12}+N_{22}\epsilon_{22}. \qquad \ldots\ldots\ldots \quad (1)$$

However, the numbers N_{11}, N_{12}, N_{22} are not independent. Let q be the coordination number of the lattice, and let us imagine that each 1 system has q arrows attached to it. Then the total number of arrows will be qN_1, and each 1–1 pair will correspond to two arrows, and each 1–2 pair to one. Thus and similarly

$$\left.\begin{aligned} 2N_{11}+N_{12}&=qN_1, \\ N_{12}+2N_{22}&=qN_2. \end{aligned}\right\} \qquad \ldots\ldots\ldots \quad (2)$$

(This is a valid approximation if boundary effects are ignored. Alternatively the equations are exact if the lattice is wrapped on a torus. The latter device is closely analogous to the use of the cyclic boundary condition in lattice dynamics, and should be asymptotically equivalent to a physical lattice for large N.) Hence for given N only two of the five quantities N_1, N_2, N_{11}, N_{12}, N_{22} are independent, and we may conveniently choose them to be N_1 and N_{12}. The energy (1) of our configuration is thus

$$\mathscr{E}(N\,;N_1,N_{12})=\tfrac{1}{2}qN\epsilon_{22}+\tfrac{1}{2}qN_1(\epsilon_{11}-\epsilon_{22})+N_{12}[\epsilon_{12}-\tfrac{1}{2}(\epsilon_{11}+\epsilon_{22})]. \quad . \quad (3)$$

The final energy in brackets in (3), $\epsilon_{12}-\frac{1}{2}(\epsilon_{11}+\epsilon_{22})$, is of basic importance in the development, and we shall denote it by ϵ. The energy of any configuration with given N_1, N_{12} can therefore be readily determined.

The fundamental problem in the theory of regular assemblies is the determination of the combinatorial factor, $g(N\,;N_1,N_{12})$, which specifies for any given lattice the number of possible configurations corresponding to given values of N_1, N_{12}. This problem can be formulated very simply, but its solution is extremely formidable. In fact only a particular class of solutions for two-dimensional lattices are so far available, and even these require sophisticated mathematical methods.

Instead of dealing with $g(N\,;N_1,N_{12})$ it is more convenient to consider the generating function

$$\begin{aligned}Z_N&=\sum_{N_1,N_{12}} g(N\,;N_1,N_{12})\exp(-\mathscr{E}/kT)\\&=z_2^{qN}\sum_{N_1,N_{12}} g(N\,;N_1,N_{12})\mu^{N_1}z^{N_{12}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)\end{aligned}$$

where

$$\mu=\exp[-\tfrac{1}{2}q(\epsilon_{11}-\epsilon_{12})/kT], \quad z=\exp(-\epsilon/kT),$$
$$z_2=\exp(-\epsilon_{22}/2kT).$$

This generating function will be interpreted physically as a partition function, but its detailed character will depend on the nature of the component systems. These systems may be atoms or molecules of two different types, in which case we have a simple model of a solid solution; Z_N will be a type of grand partition function since we are summing over all N_1, i.e. all possible concentrations. One of the species may correspond to the absence of an atom, in which case we have an assembly in which there is a certain degree of free volume, and this enables us to construct a crude model of a liquid. Alternatively the systems may consist of atomic spins, each spin being capable of two orientations, and we have a simple model of a ferromagnetic; in this case all values of N_1 are possible, and Z_N represents an ordinary partition function, the free energy being related to Z_N by

$$F_N=-kT\ln Z_N=\tfrac{1}{2}qN\epsilon_{22}-kT\ln\Lambda_N(\mu,z) \quad . \quad . \quad . \quad (5)$$

where Λ_N represents

$$\sum_{N_1,N_{12}} g(N\,;N_1,N_{12})\mu^{N_1}z^{N_{12}}.$$

We should expect the free energy to be an extensive property of the assembly and hence proportional to N for large N; thus on physical grounds Λ_N is asymptotically of the form $[\Lambda(\mu, z)]^N$ where Λ does not involve N. Similarly we should expect $g(N; N_1, N_{12})$ to be given in terms of the entropy of the assembly by Boltzmann's relation

$$S = k \ln g(N; N_1, N_{12}). \qquad \ldots\ldots\ (6)$$

Since the entropy is also an extensive property, the asymptotic form of $g(N; N_1, N_{12})$ is $f(\alpha_1, \gamma)^N$ where $\alpha_1 = N_1/N$ and $\gamma = N_{12}/N$. Quantities independent of N such as

$$\left.\begin{aligned} Z &= z_2{}^q \Lambda(\mu, z), \\ F &= \tfrac{1}{2} q \epsilon_{22} - kT \ln \Lambda(\mu, z), \end{aligned}\right\} \qquad \ldots\ldots\ (7)$$

will be referred to as the partition function or free energy *per system.*

2.2. *The Ising Model*

It is well known that a non-interacting assembly of atomic spins gives rise to paramagnetic properties which vary smoothly and continuously with temperature. The physical properties of a ferromagnetic show discontinuous behaviour at a temperature T_c known as the Curie temperature. At temperatures below T_c a ferromagnetic possesses a spontaneous magnetization, the magnetization tending to a non-zero value I_0, as the field is reduced to zero. I_0 is a continuous function of temperature which becomes zero at T_c; at temperatures above T_c there is no spontaneous magnetization, but the substance possesses a paramagnetic susceptibility which becomes infinite at T_c. The specific heat of a ferromagnetic has a λ-type singularity at the Curie point.

In fact the above properties of a ferromagnetic were accounted for in a rough way many years ago by the Weiss assumption of an internal field. But the origin of this field was not explained, and no attempt was made to relate the field to individual atomic interactions, and to solve the corresponding statistical problem.

In 1925 Ising considered an elementary model of a ferromagnetic. He assumed that each atom possessed a spin and hence a magnetic moment which could orient either parallel or anti-parallel to an external magnetic field. There is an interaction between nearest neighbour spins in the lattice, parallel spins having an interaction energy $-J$, and anti-parallel spins $+J$ $(J > 0)$. Ising hoped that this interaction might be adequate to account for the basic properties of a ferromagnetic. In fact he was able to solve the corresponding statistical problem in one dimension only, and in this case the assembly did not exhibit ferromagnetism. Subsequently Peierls (1936) was the first to show rigorously that a two- or three-dimensional model would exhibit ferromagnetism.

It will be seen that the Ising model is an example of a regular assembly, although in the presence of an external magnetic field H the interaction of each magnetic moment with the field must also be taken into account. Let m be the value of the magnetic moment. Then if the direction parallel to the field is denoted by 2 and the opposite direction by 1, the energy of an (N_1, N_{12}) configuration is given by

$$(N_1 - N_2)mH - (N_{11} + N_{22})J + N_{12}J = (2N_1 - N)mH - \tfrac{1}{2}qNJ + 2N_{12}J. \quad (8)$$

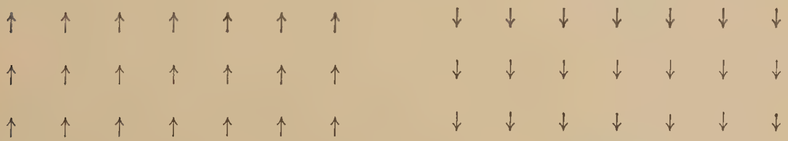
Hence by comparison with (3) and (4) we can write the partition function for the Ising model in the form

$$Z_N{}^I = \mu^{-N/2} z^{-qN/4} \Lambda_N(\mu, z), \quad . \; . \; . \; . \quad (9)$$

where now $\mu = \exp(-2mH/kT)$ and $z = \exp(-2J/kT)$. The lowest energy state corresponds to $N_1 = 0$, $N_{12} = 0$, $\Lambda_N = 1$, since $J > 0$.

In the absence of a magnetic field $\mu = 1$. It should be noted that in this case there are two equivalent lowest energy states consisting of all the spins pointing in direction 1 or in direction 2 (fig. 1). In the presence of a magnetic field this degeneracy is removed, and the lowest energy state consists of all spins pointing in direction 2. This point will be further considered when we discuss long-range order in § 3.6.4.

Fig. 1



(*a*) (*b*)

Direction 1 ↑ Direction 2 ↓

Ising model of a ferromagnetic.

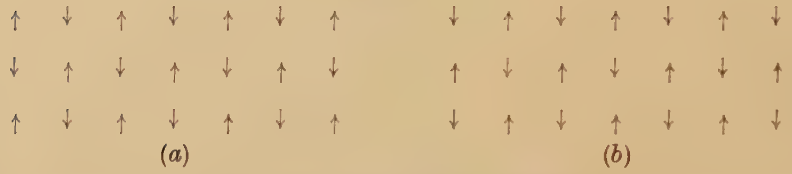
In the absence of a magnetic field (*a*) and (*b*) are equivalent lowest energy states. In the presence of a magnetic field in direction 2 (*b*) is the only lowest energy state.

The Ising interaction can be simply expressed in terms of the spin variables of the individual atoms, assuming this spin to have the value $\frac{1}{2}$. Then if s_z is the z component of the spin which can take the values $\pm\frac{1}{2}$, the interaction so far discussed between two nearest neighbour atoms i and j is equivalent to $4Js_{zi}s_{zj}$. This leads us to a natural generalization of the model to an arbitrary spin s for which s_z can take $(2s+1)$ values. The statistical problem now arising is that of a regular assembly of $(2s+1)$ components, although the interactions between these components bear a special relationship to one another. In assessing the effect of a change of s, and particularly in allowing s to become infinite (corresponding to a continuous range of possible orientations of the spin), it is convenient to normalize so that the maximum and minimum values of the interaction remain equal to $\pm J$. The generalized Ising interaction for spin s is then

$$-\frac{J}{s^2} s_{zi} s_{zj}.$$

In the past few years a good deal of attention has been devoted to the problem of anti-ferromagnetism, and if we now consider the possibility $J<0$ we are furnished with an Ising model of an anti-ferromagnetic. The formulation of the problem in (8) and (9) is still valid, but for sufficiently small H the lowest energy state corresponds to the maximum possible value of N_{12}. The value of this maximum depends on the nature of the lattice; if the lattice can be decomposed into two equivalent sub-lattices (e.g. the simple quadratic (S.Q.), simple cubic (S.C.) or body-centred cubic (B.C.C.)), the maximum corresponds to a perfect alternation, one of the sub-lattices containing spins pointing in direction 1, and the other containing spins pointing in direction 2. The maximum value of N_{12} is then $\frac{1}{2}qN$, and for this state the magnetic field terms in (8) make no contribution to the energy. However, for large H the state in which all the spins are aligned in direction 2, so that $N_1=0$, $N_{12}=0$, will have lower energy. The critical field, H_c, at which the two states have equal energies is given by $\mathfrak{m}H_c=-qJ$. For fields $H<H_c$ there are two equivalent lowest energy states, since 1 and 2 can be interchanged (fig. 2); for $H>H_c$, however, there is only one lowest energy state (fig. 1 (*b*)).

Fig. 2



Ising model of an antiferromagnetic.

(*a*) and (*b*) are equivalent lowest energy states in the presence of a magnetic field $H<H_c$.

For lattices which cannot be decomposed into two equivalent sub-lattices (e.g. the triangular or face-centred cubic (F.C.C.)) the problem of the lowest energy state is more complicated, and will be discussed further in § 3.5.4.

2.3. *Regular Solutions*

A rich variety of physical phenomena is associated with binary mixtures, many of them, such as the separation into two phases, corresponding to a discontinuous behaviour of the thermodynamic functions. In considering the properties of binary solutions we shall again use the simplest possible model capable of accounting for the basic facts. These are that under certain conditions two substances can mix freely at all concentrations, whereas under other conditions, below a certain critical temperature T_c, separation into two phases occurs at definite concentrations. Thus there is a solubility curve for any one substance in another which is a continuous function of temperature.

We shall assume that our binary mixture satisfies the conditions laid down in § 2.1 for regular assemblies, and we shall refer to solutions of this type as 'regular solutions'. This term was first introduced by Hildebrand (1929) in his pioneering work on the properties of non-ideal solutions. Hildebrand defined a regular solution as one in which the mixing of the constituents was completely random although the energies of interaction between different molecules were different. This concept proved very fruitful in a semi-empirical analysis of the properties of solutions. However, from the theoretical point of view, this can only be regarded as a first approximation, since the positions of molecules in a solution must be correlated with the interaction energies. For this reason Fowler and Guggenheim introduced the alternative definition quoted in § 2.1 which provides a simple model from which the properties of solutions can be calculated in a fundamental way. We shall always use the term in this sense, as it has become widely adopted for theoretical work (see also Hildebrand 1951, 1953, Guggenheim 1953).

In considering the partition function for a regular solution of given concentration the numbers N_1, N_2 of systems of each kind are fixed and we do not sum over these variables. Using the energy interactions of § 2.1 we may write for the partition function for a regular solution

$$Z_N{}^S = z_1{}^{qN_1} z_2{}^{qN_2} \sum_{N_{12}} g(N; N_1, N_{12}) z^{N_{12}}, \qquad . \; . \; . \; (10)$$

where $z_1 = \exp(-\epsilon_{11}/2kT)$, $z_2 = \exp(-\epsilon_{22}/2kT)$, $z = \exp(-\epsilon/kT)$. If we denote, as before, the concentration of component 1 $(= N_1/N)$ by α_1, then as N becomes large we can define a partition function per particle, independent of N, given by

$$Z^S = z_1{}^{q\alpha} z_2{}^{q(1-\alpha)} \psi(\alpha_1, z). \qquad . \; . \; . \; . \; (11)$$

It will be seen that the sum over N_{12} in (10), which is asymptotically equivalent to $[\psi(\alpha_1, z)]^N$, is equal to the coefficient of μ^{N_1} in $\Lambda_N(\mu, z)$ from (4). Hence we may write this as a contour integral

$$\frac{1}{2\pi i} \int_C \Lambda_N(\mu, z)\, d\mu / \mu^{N_1+1}$$

where C is a circle surrounding the origin. For large N the integrand has a saddle point on the real axis if there is a value of μ satisfying

$$(d/d\mu)(N \ln \Lambda - N_1 \ln \mu) = 0$$

or

$$(\mu\, d/d\mu)(\ln \Lambda) = \alpha_1. \qquad . \; . \; . \; . \; . \; (12)$$

Following the usual argument, by choosing our circle to pass through the saddle point, the major contribution to the integral comes from the neighbourhood of the saddle point, and we may write asymptotically

$$\ln \psi(\alpha, z) = \ln \Lambda(\mu, z) - \alpha_1 \ln \mu, \qquad . \; . \; . \; . \; (13)$$

where μ is now a function of α_1 and z given by (12). Hence if we know $\Lambda(\mu, z)$ as a function of the two variables μ, z and we wish to determine the regular solution function $\psi(\alpha_1, z)$ for a given concentration α_1, we must first determine the curve in the (μ, z) plane given by (12), and we then use (13) to obtain $\psi(\alpha_1, z)$. Thus the regular solution function is completely determined by a knowledge of $\Lambda(\mu, z)$.

The result (13) could equally well have been deduced by replacing the sums in (4) and (10) by their maximum terms. A more fundamental way of understanding the significance of the result is to derive it from the grand partition function (Rushbrooke 1949, Ch. 17). For a regular assembly consisting of two components the grand partition function is given by

$$\Xi(T, \lambda_1, \lambda_2) = \sum_{N_1, N_2, N_{12}} (\lambda_1 z_1{}^q)^{N_1} (\lambda_2 z_2{}^q)^{N_2} g(N; N_1, N_{12}) z^{N_{12}}, \quad . \quad (14)$$

and hence from (4), this can be put in the form

$$\Xi(T, \lambda_1, \lambda_2) = \sum_N (\lambda_2 z_2{}^q)^N \Lambda_N(\mu, z), \quad . \quad . \quad . \quad . \quad (15)$$

where μ is now equal to $\lambda_1 z_1{}^q / \lambda_2 z_2{}^q$. Since we are concerned with large values of N we can replace Λ_N by its asymptotic form Λ^N, and we find that

$$\Xi = 1/(1 - \lambda_2 z_2{}^q \Lambda). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Using the standard formulae for the G.P.F.

$$\left.\begin{aligned} N_1 &= \lambda_1\, \partial/\partial\lambda_1 \ln \Xi = \lambda_1 z_1{}^q\, \partial\Lambda/\partial\mu/(1 - \lambda_2 z_2{}^q \Lambda), \\ N_2 &= \lambda_2\, \partial/\partial\lambda_2 \ln \Xi = (\lambda_2 z_2{}^q \Lambda - \lambda_1 z_1{}^q\, \partial\Lambda/\partial\mu)/(1 - \lambda_2 z_2{}^q \Lambda). \end{aligned}\right\} \quad . \quad . \quad (17)$$

Therefore, the concentration α of component 1 which is equal to N_1/N or $N_1/(N_1+N_2)$, is given by

$$\alpha_1 = \frac{\lambda_1 z_1{}^q}{\lambda_2 z_2{}^q \Lambda} \frac{\partial\Lambda}{\partial\mu} = \mu \frac{\partial}{\partial\mu} (\ln \Lambda), \quad . \quad . \quad . \quad . \quad . \quad (18)$$

and this is in agreement with (12).

It will be seen from (15) that the function $\Lambda_N(\mu, z)$ which arose in the Ising model can be regarded as a 'restricted' grand partition function in which the ordinary partition function is summed over all possible concentrations, but the total number of systems remains fixed and equal to N. The thermodynamic properties of regular solutions can readily be determined from the G.P.F. (16).

We must now examine the lowest energy state of a regular solution of given concentration and we see from (3) that this depends on the sign of ϵ. If $\epsilon > 0$ the lowest energy state corresponds to minimizing N_{12}, and this can be achieved by dividing the assembly into two separate sections of 1 and 2 atoms with the minimum region of contact. There may be a number of independent equivalent ways of choosing this minimum region, but they will not give rise to any entropy. We may say that the lowest state of the assembly consists of two separate homogeneous phases. This sign of ϵ corresponds to the Ising model of a ferromagnetic.

If however $\epsilon < 0$ the lowest energy state of the assembly corresponds to maximizing N_{12}, which can be achieved by surrounding each 1 atom by as many 2 atoms as possible, and vice versa. This results physically in the formation of a superlattice, and hence the negative sign of ϵ is associated with order–disorder transitions in alloys; it also corresponds to the Ising model of an antiferromagnetic. The lowest energy state is degenerate, and except for a particular concentration for a given lattice gives rise to a finite value of the entropy. The determination of this entropy, and of possible lowest energy states is quite complicated, and is related to the anti-ferromagnetic in a critical field.

The problem of regular solutions with more than 2 components is much more involved. Formally a relationship with a corresponding Ising model can be established and results such as (12), (13), (15) and (16) can readily be generalized. However, the interactions between atoms in various possible spin states must be arbitrary for complete generality, and the complications arise from the different possibilities of magnitude and sign of these interactions.

2.4. *Surface Problems*

Another group of phenomena in which interactions between elementary systems can play an important role are the adsorption of gases on solids, and the growth properties of crystal surfaces. Langmuir proposed a model of an adsorbing surface as consisting of a fixed number of sites on which adsorption can take place (see Miller 1949, Ch. 2). Each gas molecule that is adsorbed occupies one site, and the sites are arranged in a regular two-dimensional array. If we assume that forces between molecules occupying sites which are not nearest neighbours can be neglected, our model is another example of a regular assembly. The forces between nearest neighbour molecules may be attractive or repulsive, and we wish to determine how the heat of adsorption and the fraction of surface covered depend on the pressure and temperature of the gas adsorbed. We must assume that thermal equilibrium is attained in the adsorbed film, and we are therefore concerned with what is usually called a mobile film.

The systems 1 and 2 of § 2.1 now correspond to occupied and vacant sites respectively. Hence we now have $\epsilon_{12} = \epsilon_{22} = 0$ in (3), and $\epsilon = -\frac{1}{2}\epsilon_{11}$. However, each adsorbed atom interacts with the surface as well as with its nearest neighbours; if we denote the energy required to evaporate one adsorbed atom from an otherwise bare surface by η, the energy of an $(N; N_1, N_{12})$ configuration is ,

$$-N_1\eta + N_{12}\epsilon. \qquad \ldots \ldots \qquad (19)$$

Hence from (4) the partition function for an adsorbed monolayer of N sites is $\Lambda_N(\mu, z)$, where now $\mu = \exp(\eta/kT)$. The fraction of occupied sites is given, as in § 2.3, by (12). The conditions of equilibrium between the layer and the adsorbing gas can be determined in the usual manner by equating the thermodynamic potentials in the two phases.

Similar considerations apply to the equilibrium structure of a crystal surface, a problem which has been discussed in detail by Burton *et al.* (1951). The 'adsorbed' layer now consists of the same molecules as the crystal, and we are interested in properties such as the rate of growth and surface roughness as functions of temperature. If we assume that only a single layer of molecules can be added the treatment is the same as for an adsorbed monolayer except that the atoms of the monolayer are the same as for the solid. If we allow for the possibility of more than one molecule becoming attached to a given site, and also allow molecules to become detached leaving vacancies, the resulting problem is somewhat similar to the generalized Ising model with arbitrary spin. However, the interaction between different levels is different, and is proportional to $|s_i - s_j|$ where s_i and s_j take positive or negative integral values or zero.

2.5. *Conclusion*

It will be seen that the properties of a regular assembly with two components are completely determined by a knowledge of a function of two variables $\Lambda(\mu, z)$ which is the partition function per spin of the Ising model in the presence of a magnetic field. There will be one particular function $\Lambda(\mu, z)$ corresponding to each type of crystal lattice. Once the nature and position of the singularities of the Ising model are known the physical results can be interpreted for any of the other problems discussed above. Our first task, therefore, is to obtain as much information as possible about $\Lambda(\mu, z)$ for different types of lattice. We need consider only values of $\mu \leqslant 1$ since values of $\mu \geqslant 1$ merely correspond to an interchange of the labels 1 and 2. However, the values of z can range from 0 to ∞, and there is a fundamental difference between the case $0 < z < 1$ $(\epsilon > 0)$ which corresponds to a ferromagnetic, and $1 < z < \infty$ $(\epsilon < 0)$ which corresponds to an antiferromagnetic.

The exact evaluation of $\Lambda(\mu, z)$ for all μ and z, has so far been possible only for a one-dimensional model. For a number of lattices in two dimensions $\Lambda(\mu, z)$ has been evaluated exactly when $\mu = 1$, and some other properties of the model have been determined exactly. In three dimensions no exact information is at present available. However, several general theorems have been established which enable us to say a good deal about the position of the singularities. In the absence of exact solutions two approaches have been used. Expansions have been developed as power series in μ, z, and $1/z$, $1/T$ (near $z = 1$); and various approximate evaluations of the function have been undertaken which correspond to ignoring certain features of the exact solution. We shall now proceed to discuss these points in further detail.

Notation for § 2

N total number of units in assembly.

q coordination number of lattice.

N_1, N_2 number of units of types 1, 2 in assembly.

$\alpha_1 = N_1/N, \quad \alpha_2 = N_2/N.$

$N_{11}\, N_{22}, N_{12}$ number of nearest neighbour pairs of various types.

$\epsilon_{11}, \epsilon_{22}, \epsilon_{12}$ energies of interaction of nearest neighbour pairs of various types.

$\epsilon = \epsilon_{12} - \frac{1}{2}(\epsilon_{11} + \epsilon_{22}).$

$z_1 = \exp[-(\epsilon_{11}/2kT)],$

$z_2 = \exp[-(\epsilon_{22}/2kT)].$

$z = \exp[-(\epsilon/kT)].$

T = absolute temperature.

k = Boltzmann's constant.

T_c = critical temperature.

$g(N; N_1, N_{12})$ = combinatorial factor, i.e. number of configurations with specified values of N_1, N_{12}.

Z_N, F_N, E_N, S_N, I_N partition function, free energy, internal energy, entropy and magnetization of assembly of N units.

Z, F, E, S, I corresponding functions per unit of the assembly.

$$\Lambda_N(\mu, z) = \sum_{N_1, N_{12}} g(N; N_1, N_{12})\mu^{N_1} z^{N_{12}}; \qquad \lim_{N\to\infty} [\Lambda_N]^{1/N} = \Lambda(\mu, z).$$

Ising Model. J = interaction energy of parallel spins.

H = external magnetic field (taken in direction 2).

m = magnetic moment of individual spin.

$z = \exp[-(2J/kT)], \quad \mu = \exp[-(2mH/kT)].$

s = total spin; s_x, s_y, s_z components of spin.

H_c = critical field for an anti-ferromagnetic.

Z_N^I, Z^I partition function for Ising model.

Z_N^S, Z^S partition function for solution.

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§ 3. EXACT METHODS AND SOLUTIONS

3.1. *One-dimensional Assemblies*

For a one-dimensional assembly of systems each having t possible energy levels a general treatment is possible which reduces the evaluation of the partition function to the determination of the largest eigenvalue of a matrix. Let $U(x_i, x_{i+1})$ denote the energy between any two systems x_i and x_{i+1} each x_i taking t possible values. We shall assume that the systems are connected in a ring so that the mth system is connected to the first; this considerably simplifies the algebra and is analogous to the cyclic boundary condition in lattice dynamics. Then the partition function for m systems is given by

$$Z_m = \sum_{x_i} \exp\left\{-\frac{1}{kT}\left[U(x_1, x_2) + U(x_2, x_3) + \ldots U(x_{m-1}, x_m) + U(x_m, x_1)\right]\right\}$$

$$= \sum_{i,\, j \ldots l=1}^{t} V_{ij} V_{jk} \ldots V_{kl} V_{li}, \qquad \ldots \ldots \ldots \quad (1)$$

where $V_{ij} = \exp(-U_{ij}/kT)$ corresponds to the interaction between neighbouring systems in states i and j respectively. The elements V_{ij} thus form a $t \times t$ matrix $\mathbf{V}$ and the continued product (1) will be readily identified as the trace of $\mathbf{V}^m$. Thus if $\lambda_1, \ldots \lambda_t$† are the latent roots of $\mathbf{V}$,

$$Z_m = \lambda_1^{\,m} + \lambda_2^{\,m} + \ldots + \lambda_t^{\,m}. \qquad \ldots \ldots \quad (2)$$

For sufficiently large m only the largest root λ_1 is significant, and we may identify Z_m with $\lambda_1^{\,m}$, and the partition function per system with λ_1. Even if the largest root is p-fold degenerate this result still holds since $p^{1/m}$ tends to 1 as $m \to \infty$. It should be noted that if the interaction V_{ij} is symmetric in i and j, then the matrix $\mathbf{V}$ is symmetric; also $(\mathbf{V}^m)_{ii}$, the ith diagonal element of $\mathbf{V}^m$ is proportional to the probability that a particular system is in state i.

The above method of treating a class of one-dimensional assemblies was suggested independently by Kramers and Wannier (1941), Lassettre and Howe (1941), and Montroll (1941). It can be applied to systems with a continuous range of energy levels, but the eigenvalues in (2) must now be replaced by the eigenvalues of an integral equation

$$\int \exp\left[-U(y, z)/kT\right] a(y)\, dy = \lambda a(z). \qquad \ldots \ldots \quad (3)$$

In this case the number of eigenvalues will no longer be finite and additional care with the pure mathematics is needed to establish the conclusions.

3.2. *Application to the Ising Model*

3.2.1. *The simple Ising chain*

For the simple one-dimensional Ising model in the absence of a magnetic field the application is immediate. There are two states for each system and $\mathbf{V}$ is a 2×2 matrix; for a generalized r-state model $\mathbf{V}$ would be an

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† These should not be confused with λ_1, λ_2 of § 2.3.

$r \times r$ matrix. However, in the presence of a magnetic field, the interaction with the field must also be taken into account, and to preserve the symmetry of the treatment it is sometimes convenient to attribute half of the interaction of each of the two neighbouring systems x_i and x_{i+1} to $U(x_i, x_{i+1})$. We thus write for the generalized Ising model of spin s

$$U(x_i, x_{i+1}) = -\frac{J}{s^2} s_{z,i} s_{z,i+1} - \frac{\mathscr{m}H}{2s}(s_{z,i} + s_{z,i+1}), \quad . \quad . \quad . \quad (4)$$

and in particular for the two-state model, using the notation of § 2.2:

$$\mathbf{V} = \begin{vmatrix} \mu^{-1/2} z^{-1/2} & z^{1/2} \\ z^{1/2} & \mu^{1/2} z^{-1/2} \end{vmatrix} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and

$$\Lambda(\mu, z) = \tfrac{1}{2}\{(1+\mu) + \sqrt{[(1-\mu)^2 + 4\mu z^2]}\}. \quad . \quad . \quad . \quad (6)$$

The two eigenvalues λ_1, λ_2 correspond to positive and negative signs of the root.

Despite the simplicity of this result a number of interesting and useful conclusions can be drawn from it. In the absence of a magnetic field ($\mu = 1$) the partition function reduces to $z^{-1/2} + z^{1/2}$ (see (9), § 2). There is no singularity in the partition function, which is equivalent to that of an assembly of non-interacting systems each having two independent energy levels. The specific heat is equal to $mk(J/kT)^2 \operatorname{sech}^2(J/kT)$, and this is drawn as a function of temperature in fig. 1. Although the specific heat has a maximum at $kT = 0{\cdot}833\,J$ this maximum is not associated with any peculiar behaviour of the magnetic properties of the chain.

In fact the magnetization of the chain per spin is given by

$$\begin{aligned} I = kT\,\partial/\partial H\,[\ln Z] &= -2\mathscr{m}\mu\,\partial/\partial\mu\,[-\tfrac{1}{2}\ln\mu + \ln\Lambda] \\ &= \mathscr{m}[1 - 2\mu\Lambda_\mu/\Lambda]. \quad . \quad . \quad . \quad . \quad (7) \end{aligned}$$

Now,

$$\Lambda_\mu = \tfrac{1}{2} + \frac{-2(1-\mu) + 4z^2}{4\sqrt{[(1-\mu)^2 + 4\mu z^2]}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and hence as $H \to 0$, and $\mu \to 1$, $\Lambda_\mu \to \tfrac{1}{2}(1+z)$, and $I \to 0$ for all z. Thus the magnetization tends to zero as the field tends to zero for all temperatures, and there is no spontaneous magnetization. However, if we proceed to determine the susceptibility we do find evidence of peculiar behaviour at $T = 0$. The susceptibility is given by

$$\chi = \partial I/\partial H = -2\mu\mathscr{m}/kT\,\partial I/\partial\mu = \frac{4\mathscr{m}^2}{kT}[\mu\Lambda_\mu/\Lambda + \mu^2(\Lambda_{\mu\mu}/\Lambda - \Lambda_\mu{}^2/\Lambda^2)], \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and as $\mu \to 1$, this is equal to

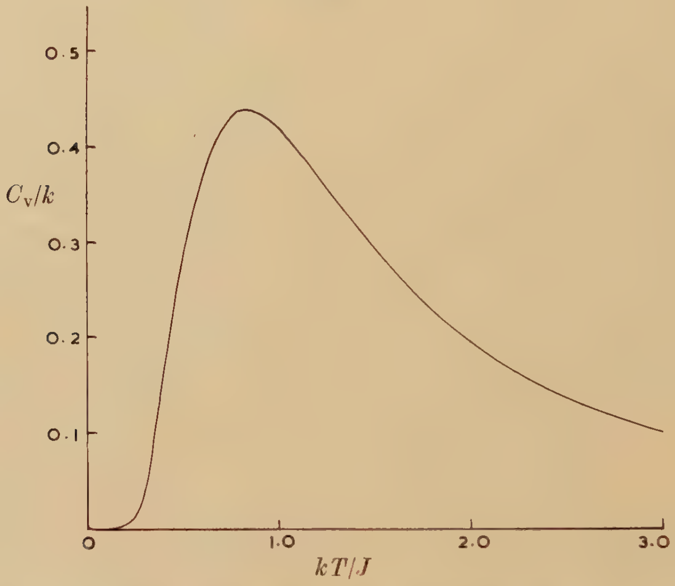
$$(4\mathscr{m}^2/kT)[\tfrac{1}{4} + \Lambda_{\mu\mu}/\Lambda] = \mathscr{m}^2/kT \exp(2J/kT). \quad . \quad . \quad . \quad (10)$$

Thus when $J > 0$ (i.e. for a ferromagnetic) the susceptibility becomes infinite at $T = 0$. If we now examine the expression (6) we see that a power series expansion in μ and z is possible for $\Lambda(\mu, z)$ about any point for which

$\mu \neq 1$, $z \neq 0$. No such expansion is possible, however, about $\mu = 1$, $z = 0$, which corresponds to zero temperature and zero magnetic field. For this reason it is often convenient to describe a linear chain as a ferromagnetic whose Curie point has gone to zero.

We can also learn something of the behaviour of an antiferromagnetic from the solution for the linear chain. In the absence of a magnetic field the partition function is the same as for a ferromagnetic. However, the magnetic behaviour is very different. The susceptibility in zero field is given by (10) but J is now negative; hence it tends to zero as $T \to 0$ and as $T \to \infty$ and has a maximum at a temperature $2J/k$. The behaviour at $T = 0$ is no longer peculiar in zero field but in a critical field $H_c = 2J/m$ (see end of § 2.2). Let us consider the lowest energy antiferromagnetic configuration, which consists of alternating spins on each of two sub-lattices pointing respectively in the direction of, or in the opposite direction to, the field. In the critical field any spin of the latter sub-lattice can be overturned without change of energy. Hence the lowest energy state has degeneracy at least $2^{(1/2)m}$. But in fact there is further degeneracy in the assembly, since if any two neighbouring spins of the second sub-lattice have overturned to point in the direction of the field, the spin of the first sub-lattice which lies between them can also be overturned with no change in energy (fig. 2). We can calculate the actual degeneracy in the

Fig. 1



Specific heat of a linear Ising chain. The maximum does not correspond to anomalous thermodynamic behaviour.

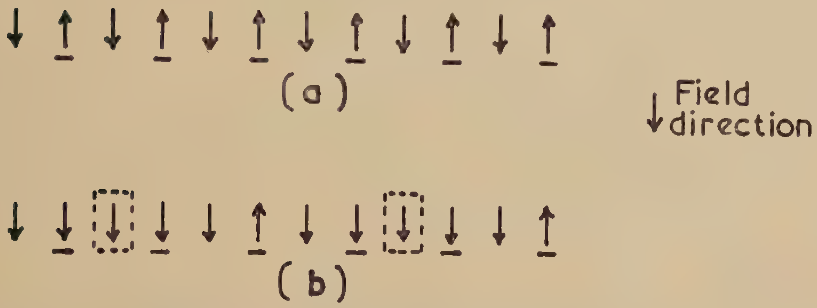
critical field from (6), remembering that when $mH=-2J$, $\mu z^2=1$. We have, for the entropy,

$$S=-\partial F/\partial T=k\ln\Lambda+kT\,\partial/\partial T\,(\ln\Lambda), \quad . \quad . \quad . \quad (11)$$

and, when $\mu z^2=1$ the second term gives zero as $T\rightarrow 0$. Hence

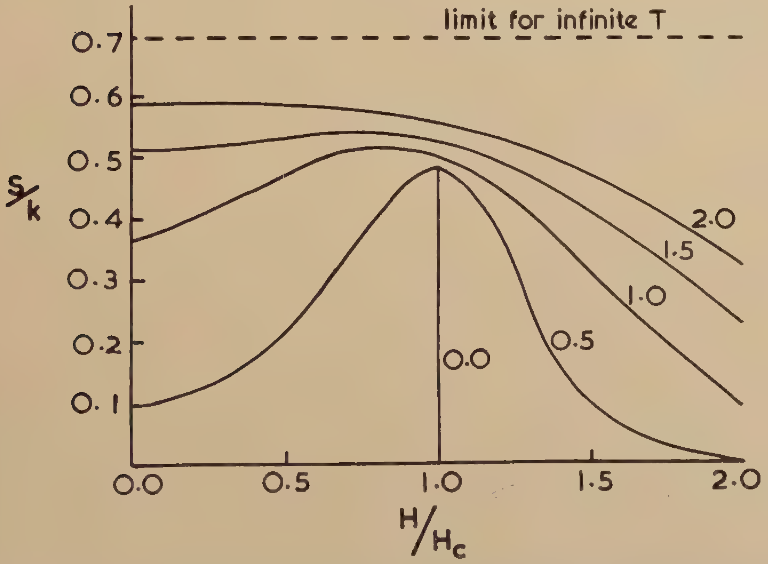
$$S_c\rightarrow k\ln\left(\frac{1+\sqrt{5}}{2}\right)=k\ln(1\cdot 618).$$

Fig. 2



Lowest energy states of an antiferromagnetic chain in a critical field. (*a*) Any of the underlined spins can overturn without change of energy. (*b*) if two neighbouring underlined spins in (*a*) have overturned the intermediate ringed spin can overturn without change of energy.

Fig. 3



Entropy of an antiferromagnetic chain as a function of magnetic field. The initial field breaks up the alternating order and increases the entropy. When the field increases sufficiently ferromagnetic ordering takes place, and the entropy decreases.

At $T=0$ if H is slightly less than, or slightly greater than H_c the entropy is zero again. Thus the entropy as a function of magnetic field consists of an isolated line at $H=H_c$. At temperatures different from zero this line spreads out into a curve which becomes broader as the temperature rises, but the maximum is still recognizable at quite elevated temperatures (fig. 3). This corresponds to the physical fact that a magnetic field breaks up the alternating order of the spins, and hence increases the disorder of the chain; only when the field increases sufficiently to line up the spins does the order again increase. As might be expected the susceptibility in the critical field also has anomalous behaviour at low temperatures; it is easy to show from (9) that $\chi_c \to \sqrt{5}m^2/25kT$.

The low temperature behaviour discussed in the previous paragraph is clearly in disagreement with the third law of thermodynamics; such a system giving rise to a finite entropy at the absolute zero for a particular magnetic field could be used to reach absolute zero (Simon 1956). From this we may conclude that the Ising interaction is not a rigorously correct form of physical interaction, and for a real physical system additional interaction terms would enter to split the degeneracy in a critical field.

It would be of interest to investigate the corresponding behaviour of a linear chain with a Heisenberg interaction, $J\boldsymbol{\sigma}_i . \boldsymbol{\sigma}_j$ between neighbouring spins (where the $\boldsymbol{\sigma}_i$ are the Pauli spin operators) since this interaction has a sounder physical basis. Although a formal solution exists to this problem (Bethe 1931, Hulthen 1938) it has not so far been possible to use this solution to calculate physical properties such as those discussed above. The most general interaction between spins which takes account of magnetic anisotropy is of the form $A\sigma_{xi}\sigma_{xj}+B\sigma_{yi}\sigma_{yj}+C\sigma_{zi}\sigma_{zj}$, and the Ising interaction is thus an approximation corresponding to extreme magnetic anisotropy (A and B negligible compared with C). For certain substances (e.g. FeF_2) this can be regarded as a reasonable approximation; however, at sufficiently low temperatures the terms A and B can no longer be neglected.

Before leaving the one-dimensional solution we should draw attention to an interesting difference between the ferromagnetic and antiferromagnetic solutions when m is odd. The exact solution for the partition function in the absence of a magnetic field is, by (2) and (6)

$$Z_m=(z^{-1/2}+z^{1/2})^m+(z^{-1/2}-z^{1/2})^m. \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

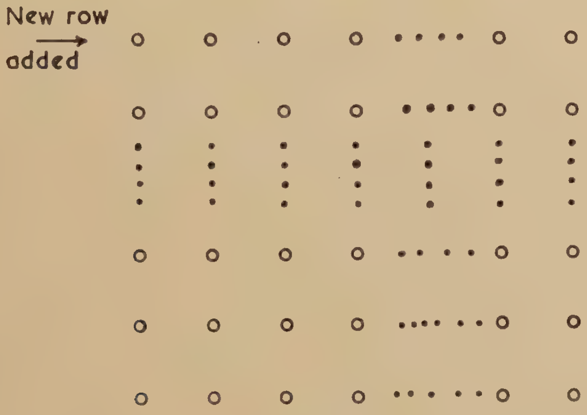
When m is even this expression is invariant when J is replaced by $-J$. However, when m is odd the second factor is multiplied by -1, and this corresponds to the physical fact that one spin must be a misfit in the ordered antiferromagnetic chain. Thus the lowest energy state for the antiferromagnetic case has energy $(m-2)J$ because of the energy of the misfit spin, and is $2m$-fold degenerate because of the position which this misfit can occupy. However, at any temperature different from zero the second term in (12) is negligible compared with the first for large m, and the ferromagnetic and antiferromagnetic solutions are identical.

Thus the misfit spin contributes to the partition function only at the absolute zero. We shall pursue this point further for the two-dimensional model in § 3.5.1.

3.2.2. *The two- and three-dimensional models*

The same method can be applied to the two- and three-dimensional Ising models, building up the lattice by adding one row or one layer at a time. Thus for a two-dimensional lattice consisting of n rows as shown in fig. 4, each system of § 3.1 consists of a row of n spins with 2^n possible energy states. Thus the matrix $\mathbf{V}(\equiv \mathbf{V}_n)$ is of order 2^n (r^n for the generalized model). The treatment of § 3.1 will apply if the systems are joined to form an anchor ring. Similarly for a three-dimensional lattice consisting of $p \times n$ layers joined together to form a torus the matrix $\mathbf{V}$ is of order 2^{pn}. It should be emphasised that the matrix $\mathbf{V}(\equiv \mathbf{V}_{p,n})$ can be chosen to be symmetric, and all its elements are positive.

Fig. 4



Each added unit consists of a row of n spins.

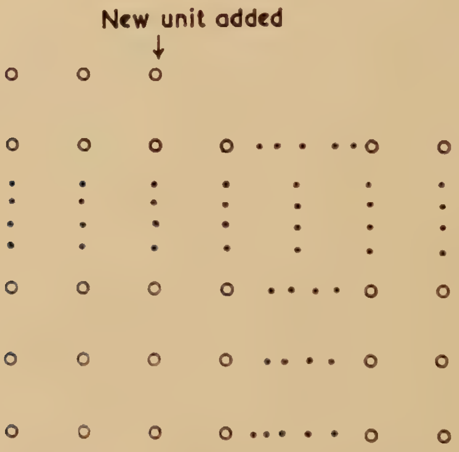
However, it is quite a complicated matter to write down the appropriate matrices $\mathbf{V}_n$, $\mathbf{V}_{p,n}$ for particular values of p and n, and these matrices can be decomposed into product matrices of simple characteristic structure. This can most readily be demonstrated by the use of the 'screw transformation' introduced by Kramers and Wannier (1941). In the two-dimensional lattice consisting of n rows we now build up successive rows by adding one unit at a time instead of a whole row, as shown in fig. 5. The treatment of § 3.1 can be modified to deal with this, although the symmetry of the matrix must now be sacrificed; $\mathbf{V}_n$ can be written in the form $\mathbf{A}_n^{\,n-1}\mathbf{B}_n^{\,n}$ where $\mathbf{A}_n$, $\mathbf{B}_n$ have simple characteristic structure.

The $\mathbf{B}_n$ matrix corresponds to an end effect, and if successive columns are linked together to form a screw, the nth elements of any row being linked to the first element of the succeeding row, only the matrix $\mathbf{A}_n$

remains. It seems very likely that as $n \to \infty$ the effect of the screw linkage will become negligible, and the partition function for the two-dimensional quadratic lattice will be given by the largest eigenvalue of $\mathbf{A}_n$. An analogous transformation can also be carried out for the three-dimensional model (for further details see Domb 1949 a).

Despite the apparent simplicity of structure of these matrices little progress has been made in reducing them or determining their eigenvalues except for two-dimensional lattices in the absence of a magnetic field where other solutions are also available (Newell 1950). They were instrumental in leading Kramers and Wannier (1941) to the exact location of the Curie point of the simple quadratic lattice, and they have been used to derive power series expansions for the partition function (Ashkin and Lamb 1943, Domb 1949 b). However, these can usually be obtained more easily by combinatorial methods which will be described in § 5.

Fig. 5



Each added unit consists of a single spin.

3.2.3. *Conditions for the existence of singularities*

The matrices $\mathbf{V}$ introduced in the previous section are finite and symmetric; their elements are simple analytic functions of μ and z ($\mu, z \neq 0$) which are bounded and have bounded derivatives. To determine the derivatives of the largest eigenvalue in the neighbourhood of a given point we can use standard perturbation theory as developed for example in quantum mechanics (e.g. Mott and Sneddon § 18.1). At any given point the matrix has eigenvalues $\lambda_1, \ldots \lambda_l$ and corresponding eigenvectors $\xi_1, \ldots \xi_l$, and even if the eigenvalues are not all distinct, because of the symmetry of the matrix the eigenvectors can be chosen to be independent and orthogonal. The changes in λ_1 and $\boldsymbol{\xi}_1$ as a result of a change $\delta\mathbf{V}$ in $\mathbf{V}$ are given by

$$\left.\begin{aligned}\delta\lambda_1&=\boldsymbol{\xi}_1'\delta\mathbf{V}\boldsymbol{\xi}_1,\\ \delta\boldsymbol{\xi}_1&=\sum_{i=2}^{t}\boldsymbol{\xi}_1'\delta\mathbf{V}\boldsymbol{\xi}_i/(\lambda_1-\lambda_i),\end{aligned}\right\}\begin{aligned}&+\text{second-order}\\ &\text{terms in } \delta\lambda,\ \delta\boldsymbol{\xi}.\end{aligned} \quad . \quad . \quad . \quad (13)$$

Thus if the largest eigenvalue is non-degenerate both $\delta\lambda_1$ and $\delta\boldsymbol{\xi}_1$ will be of the first order, from (13), and the limits to which $\delta\lambda_1/\delta\mu$, $\delta\lambda_1/\delta z$ tend will be independent of the paths of $\delta\mu$, δz. Hence λ_1 will be an analytic function without singularities.

An alternative method of deriving this result is to consider directly the characteristic equation for $\mathbf{V}$. It is easy to see that this is of the form

$$f(\lambda;\ \mu,z)=\sum_{i=0}^{t}\lambda^i\phi_i(\mu,z)=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where $\phi_i(\mu,z)$ are simple analytic functions of μ and z $(\mu,z\neq 0)$. Hence

$$\partial\lambda_1/\partial z=-(\partial f/\partial z)/(\partial f/\partial\lambda)_{\lambda=\lambda_1}; \quad . \quad . \quad . \quad . \quad . \quad (15)$$

λ_1 will only be singular if $\partial f/\partial\lambda=0$, i.e. if $\lambda=\lambda_1$ is a repeated root of $f\,(\lambda;\ \mu,z)=0$.

Now there is a theorem of Perron (1907) and Frobenius (1908) which states that finite matrices with positive elements have largest eigenvalues which are simple. From this we draw the conclusion that any lattice which is infinite in one dimension only will have no singularities. The argument can readily be generalized to any forces of finite range. A singularity can only arise for such forces if the lattice is infinite in at least two dimensions.

The proof given by Frobenius† is involved and depends on the use of mathematical induction. In our applications only symmetric matrices need be considered, and a simpler proof can be constructed. Since the theorem is of some significance in the theory of cooperative phenomena we give such a proof in Appendix I.

3.3. *Order and Long-range Order*

Let $\langle\alpha_1\rangle$ and $\langle\alpha_2\rangle$ represent the mean fractions of spins pointing in directions 1 and 2 respectively at any given temperature. Consider any two sites in the lattice which we denote by a, b; it is of interest to know whether the spins on these sites are correlated, and we wish to find a method of defining the correlation precisely. Let $\langle\alpha_{11}{}^{ab}\rangle$ $\langle\alpha_{22}{}^{ab}\rangle$ $\langle\alpha_{12}{}^{ab}\rangle$ $\langle\alpha_{21}{}^{ab}\rangle$ represent the mean fractions of pairs of spins on sites equivalent to a and b being occupied at any given temperature by 1–1, 2–2, 1–2, 2–1 respectively. Then it is clear that the following relations hold

$$\left.\begin{aligned}\langle\alpha_{11}{}^{ab}\rangle+\langle\alpha_{12}{}^{ab}\rangle&=\langle\alpha_1\rangle,\\ \langle\alpha_{21}{}^{ab}\rangle+\langle\alpha_{22}{}^{ab}\rangle&=\langle\alpha_2\rangle,\\ \langle\alpha_{12}{}^{ab}\rangle=\langle\alpha_{21}{}^{ab}\rangle,\quad \langle\alpha_1\rangle+\langle\alpha_2\rangle&=1.\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Hence if $\langle\alpha_1\rangle$ and $\langle\alpha_2\rangle$ are given $\langle\alpha_{11}{}^{ab}\rangle$ $\langle\alpha_{12}{}^{ab}\rangle$ $\langle\alpha_{22}{}^{ab}\rangle$ depend on only one parameter, and this can be used to define the order between the sites a and b. If there were no correlation between the spins on a and b we should have

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† Alternative proofs have been constructed recently—see Gantmacher (1959), Bellman (1960).

$$\langle \alpha_{11}{}^{ab} \rangle = \langle \alpha_1 \rangle^2, \quad \langle \alpha_{12}{}^{ab} \rangle = \langle \alpha_1 \rangle \langle \alpha_2 \rangle, \quad \langle \alpha_{22}{}^{ab} \rangle = \langle \alpha_2 \rangle^2. \quad . \quad (17)$$

Thus in general we shall write

$$\langle \alpha_{11}{}^{ab} \rangle = \langle \alpha_1 \rangle^2 (1 + \mathscr{S}_{ab}),$$

and hence from (16)

$$\left.\begin{aligned} \langle \alpha_{12}{}^{ab} \rangle &= \langle \alpha_1 \rangle [\langle \alpha_2 \rangle - \langle \alpha_1 \rangle \mathscr{S}_{ab}], \\ \langle \alpha_{22}{}^{ab} \rangle &= \langle \alpha_2 \rangle^2 + \langle \alpha_1 \rangle^2 \mathscr{S}_{ab} \end{aligned}\right. \quad . \quad . \quad . \quad . \quad (18)$$

where for convenience $\langle \alpha_1 \rangle$ is taken $\leqslant \frac{1}{2}$. If $\mathscr{S}_{ab} = 0$ there is no correlation between the spins, and the deviation of $\mathscr{S}_{ab}$ from zero provides a measure of the correlation.

We now enquire what happens to $\mathscr{S}_{ab}$ as the distance between a and b becomes very large. If $\mathscr{S}_{ab}$ tends to a limit $\mathscr{S}_\infty$ different from zero we say that long-range order is present in the lattice. To secure agreement with the usual definition of long-range order we must write $\mathscr{S}_\infty = R^2$, and R is a measure of the long-range order. The advantage of $\mathscr{S}_\infty$ is that it can be both positive and negative, and hence for an ordered antiferromagnetic array its limiting behaviour consists of an alternation in sign as the number of steps between the two sites changes from odd to even. If we are to use R, the definition (18) is valid for an antiferromagnetic array only for sites separated by an even number of steps, and a re-definition is required for an odd number of steps.

The above definitions of order and long-range order are immediately adaptable to solutions and superlattices containing two components of fixed concentrations. If more components are present a number of additional parameters are required to specify the order of the lattice. This definition has the advantage that if does not refer to any particular basic arrangement of spins on the lattice; hence the concept of 'right' and 'wrong' atoms is not required, and equivalent ordered states are automatically taken into account.

For the Ising model of spin $\frac{1}{2}$ it is convenient to introduce variables σ_i for each lattice point i where the z-component of spin, $s_{zi} = \frac{1}{2}\sigma_i$; σ_i takes the values ∓ 1 according as the ith spin is pointing in direction 1 or 2. The correlations can then be expressed in terms of the averages $\langle \sigma_a \rangle$, $\langle \sigma_a \sigma_b \rangle$; it is easy to show that

$$\left.\begin{aligned} \langle \sigma_a \rangle &= \langle \alpha_2 \rangle - \langle \alpha_1 \rangle, \\ \langle \sigma_a \sigma_b \rangle &= [\langle \alpha_1 \rangle - \langle \alpha_2 \rangle]^2 + 4\langle \alpha_1 \rangle^2 \mathscr{S}_{ab} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (19)$$

These formulae can be generalized to provide a definition of order for the Ising model with arbitrary spin s in terms of $\langle s_{za} \rangle$ and $\langle s_{za} s_{zb} \rangle$; and for the Heisenberg model for which the s_{za} for individual sites are no longer constants of the motion, and one cannot therefore refer to a particular spin as pointing in direction 1 or 2.

The concept of order is particularly useful for understanding the behaviour of cooperative assemblies. One of the most important physical conclusions of our investigation will be that the propagation of order to large distances does not require long-range forces. Even crystals with nearest neighbour forces can manifest long-range order which is then destroyed by thermal agitation at certain critical temperatures.

3.3.1. *Condition for long-range order*

We have seen in § 3.1 that the partition function of a linear chain of a large number m of systems each having t possible energy levels, is given by the largest eigenvalue of a matrix $\mathbf{V}$; and that the probability distribution of any particular system among the levels at a given temperature is determined by the diagonal elements of $\mathbf{V}^m$. In § 3.2.2 we have shown how this can be adapted to the two- and three-dimensional Ising models; for an n-rowed simple quadratic lattice $t=2^n$, and for a $p \times n$ simple cubic lattice $t=2^{pn}$. We shall now investigate the eigenvectors and eigenvalues of the matrix $\mathbf{V}$, and derive their physical interpretation.

$\mathbf{V}$ can be taken as symmetric; therefore its eigenvalues are all real, and its left and right-hand eigenvectors are the same. Let us denote the eigenvalues by $\lambda_1, \lambda_2 \ldots \lambda_t$, and the normalized eigenvectors by $\boldsymbol{\xi}_1 \ldots \boldsymbol{\xi}_t$; the latter can always be chosen to be orthogonal even if there is degeneracy in the eigenvalues. Let $\boldsymbol{\alpha}$ denote the vector with a 1 in the αth position and zero elsewhere. Then

$$\boldsymbol{\alpha} = \sum_{i=1}^{t} \alpha_i \boldsymbol{\xi}_i \quad \ldots \ldots \ldots \quad (20)$$

where α_i is the αth component of $\boldsymbol{\xi}_i$. Hence the αth diagonal element of $\mathbf{V}^m$, which is equal to $\boldsymbol{\alpha}' \mathbf{V}^m \boldsymbol{\alpha}$, is

$$\left(\sum_{j=1}^{t} \alpha_j \boldsymbol{\xi}_j'\right)\left(\sum_{i=1}^{t} \lambda_i^m \alpha_i \boldsymbol{\xi}_i\right) = \sum_{i=1}^{t} \alpha_i^2 \lambda_i^m, \quad \ldots \ldots \quad (21)$$

and the probability of a given system being in state α is equal to

$$\sum_{i=1}^{t} \alpha_i^2 \lambda_i^m \Big/ \sum_{i=1}^{t} \lambda_i^m. \quad \ldots \ldots \ldots \quad (22)$$

When m is large only the largest eigenvalue need be considered. If this is simple, the probability reduces to α_1^2, i.e. the squares of the components of the eigenvector $\boldsymbol{\xi}_1$ are equal to the probabilities of the systems being in the state corresponding to this component. If it is degenerate we must sum α_1^2 over all the independent eigenvectors corresponding to the largest eigenvalue. For the two- and three-dimensional Ising models, we may be interested in a particular spin of a given layer, and we must then sum over all states of the layer consistent with the spin having this value.

We now consider the probability of two systems in layers l and h being simultaneously in states α and β respectively. This probability is proportional to

$$\sum_{i,j,\ldots r=1} V_{\alpha i} V_{ij} \ldots V_{k\beta} V_{\beta l} \ldots V_{r\alpha} \quad \ldots \ldots \quad (23)$$

and this is equal to the $\alpha\beta$ component of $\mathbf{V}^h \times$ the $\beta\alpha$ components of $\mathbf{V}^{m-h}$. Following the same procedure as in (21) we find that $\alpha\beta$ component of $\mathbf{V}^h$ is equal to

$$\sum_{i=1}^{t} \alpha_i\beta_i\lambda_i^h \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Hence the required probability is

$$\left(\sum_{i=1}^{t} \alpha_i\beta_i\lambda_i^h\right)\left(\sum_{j=1}^{t} \alpha_j\beta_j\lambda_j^{m-h}\right)\Big/ \sum_{i=1}^{t} \lambda_i^m. \quad . \quad . \quad . \quad . \quad (25)$$

When h, m are large the behaviour is again dominated by the largest eigenvalue, but we must consider separately the cases when it is simple or degenerate. If the largest eigenvalue λ_1 is simple (25) reduces to $\alpha_1{}^2\beta_1{}^2$, which is the product of the probabilities for the two layers separately; there is thus no correlation between these layers, and long-range order is absent. If on the other hand the largest eigenvalue is degenerate, let us suppose, for example, that there are two independent eigenvectors which we denote by $\boldsymbol{\xi}_+$ and $\boldsymbol{\xi}_-$. (25) now reduces to $(\alpha_+\beta_+ + \alpha_-\beta_-)^2$ whereas the probabilities for the separate layers are $\alpha_+{}^2 + \alpha_-{}^2$, $\beta_+{}^2 + \beta_-{}^2$. We thus see that there is a correlation between the layers, and long-range order is present. If we wish to evaluate this long-range order for the Ising model using the formulae of the previous section for correlations between individual spins, we must sum over all configurations of the layers consistent with the spins having particular values. We may thus draw the general conclusion that the condition for long-range order to be present in an assembly is that the largest eigenvalue of the corresponding matrix is degenerate; the long-range order is determined by the largest eigenvectors.

If we wish to know the value of the order at any finite distance we must study the remaining eigenvalues and eigenvectors; for large m all terms other than those corresponding to λ_1 in the second bracket of (25) can be neglected. The formula for the joint probability of layers 1 and h then reduces to

$$\alpha_1\beta_1\left[\alpha_1\beta_1 + \sum_{i=2} (\lambda_i/\lambda_1)^h\alpha_i\beta_i\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

if λ_1, is simple, or

$$[\alpha_+\beta_+ + \alpha_-\beta_-]\left[\alpha_+\beta_+ + \alpha_-\beta_- + \sum_{i=2}^{t} (\lambda_i/\lambda_1)^h\alpha_i\beta_i\right] \quad . \quad . \quad . \quad (27)$$

if λ_1 is degenerate. In the first case the ratio (λ_2/λ_1) provides a rough estimate of the distance to which order extends. We may thus summarize by saying that the remaining eigenvalues and eigenvectors of $\mathbf{V}$ determine the 'propagation of order' in the lattice. This concept was first introduced by Zernicke (1938), and we have here largely followed the development of Ashkin and Lamb (1943).

3.4. *Transformation Properties of the Ising Model*

3.4.1. *General transformations*

We have seen from § 2 (5) that the partition function for the Ising model can be expressed as a sum of terms each of which represents a configuration with a given number, N_1, of spins pointing in direction 1, and a given number, N_{12}, of 1–2 nearest neighbour links. There is complete symmetry between directions 1 and 2; thus if we replace H by $-H$ the partition function must be unchanged. Hence from § 2 (9)

$$\left.\begin{aligned} \mu^{-(1/2)N}\Lambda_N(\mu, z) &= \mu^{(1/2)N}\Lambda_N(\mu^{-1}, z) \\ \text{or}\qquad \mu^{-(1/2)}\Lambda(\mu, z) &= \mu^{(1/2)}\Lambda(\mu^{-1}, z). \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

If we start with the lowest energy state at the absolute zero, we can classify the configurations in terms of increasing deviation from the lowest energy state as more spins overturn, and more links are broken. We shall now confine attention to lattices such as the S.Q., S.C. and B.C.C. which can be divided into two equivalent sub-lattices. In the absence of a magnetic field, there is an exact correspondence in energy between the configurations of a ferromagnetic $(J>0)$ and those of an antiferromagnetic $(J<0)$. This means that the partition function in the absence of a magnetic field for these lattices must be invariant under the transformation $J \to -J$, and hence from § 2 (9):

$$\left.\begin{aligned} z^{-qN/4}\Lambda_N(1, z) &= z^{qN/4}\Lambda_N(1, z^{-1}), \\ z^{-q/4}\Lambda(1, z) &= z^{q/4}\Lambda(1, z^{-1}). \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

Using the σ_i introduced in the previous section the partition function of the Ising model for any lattice can be written in the form

$$Z_N{}^I = \exp\left\{(J/kT)\left[\sum \sigma_i\sigma_j + \frac{mH}{kT}\sum \sigma_i\right]\right\}, \quad . \quad . \quad . \quad (30)$$

where the sum must be taken over 2^N possible values of the σ_i for all the N lattice points, and i, j are nearest neighbours; we can thus consider the first term in (30) as a sum over all nearest neighbour links in the lattice. Clearly the σ variables commute and (30) can be written as a product

$$Z_N{}^I = \prod_{i,j} \exp K(\sigma_i\sigma_j) \prod_i \exp\left(\frac{mH}{kT}\sigma_i\right) (K = J/kT). \quad . \quad . \quad (31)$$

The $\sigma_i\sigma_j$ satisfy the relation

$$(\sigma_i\sigma_j)^2 = (\sigma_i\sigma_j)^4 \ldots = 1, \ (\sigma_i\sigma_j) = (\sigma_i\sigma_j)^3 = (\sigma_i\sigma_j)^5 = \ldots,$$

and hence we can write

$$\exp(K\sigma_i\sigma_j) = \cosh K + \sigma_i\sigma_j \sinh K. \quad . \quad . \quad . \quad . \quad . \quad (32)$$

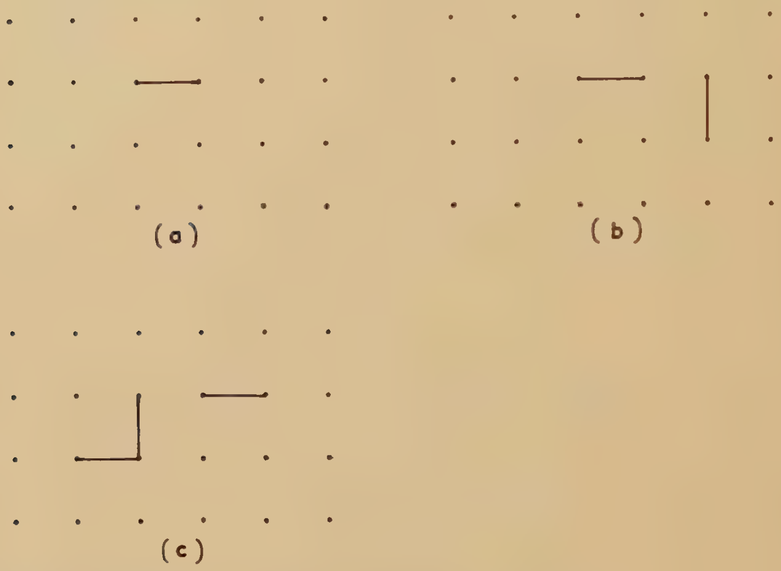
We can expand the first product in (31) as follows (van der Waerden 1941)

$$\begin{aligned} \prod_{ij} (\cosh K + \sigma_i\sigma_j \sinh K) &= \cosh^{\mathscr{N}} K \prod_{ij} [1 + \sigma_i\sigma_j \tanh K] \\ &= \cosh^{\mathscr{N}} K \sum_{ij\ldots k} [1 + (\tanh K)(\sigma_i\sigma_j) \\ &\qquad + (\tanh^2 K)(\sigma_i\sigma_j)(\sigma_k\sigma_l) + \ldots] \quad . \quad . \quad . \quad . \quad (33) \end{aligned}$$

where $\mathcal{N}$ is the number of nearest neighbour links in the lattice. This can now be interpreted topologically. The first term $\sigma_i\sigma_j$ corresponds to any one of the $\mathcal{N}$ nearest neighbour links in the lattice; the second term corresponds to any non-identical pair of nearest neighbour links and there will be $\mathcal{N}(\mathcal{N}-1)2!$ such pairs; similarly for higher terms (see fig. 6).

The series development (33) can be used as a basis for a high temperature expansion of the partition function in a magnetic field, and will be discussed further in § 3.6.2. It should be noted that there is no approximation in (33), and provided the sum is carried on to the $\mathcal{N}$th term the result is valid for any aggregate of spins.

Fig. 6



Typical contributions to the high temperature expansion.
(*a*) First term $\mathcal{N}$ contributions;
(*b*) Second term $\mathcal{N}(\mathcal{N}-1)/2!$ contributions;
(*c*) Third term $\mathcal{N}(\mathcal{N}-1)(\mathcal{N}-2)/3!$ contributions.

We now particularize to the case $H=0$, and this introduces a substantial simplification, since the second product in (31) becomes unity. Also any configuration with an odd number of lines meeting at a vertex will have an odd σ_i left in the summation, and will give zero contribution. Hence the only non-zero contributions arise from closed polygons each vertex of which is the meeting point of 2, 4, 6 ... nearest neighbour links. Typical polygons are shown in fig. 7.

Any such polygon gives a contribution 2 for each vertex when we sum over the appropriate σ_i; the σ_i at all remaining vertices likewise give a factor 2, and we obtain a total factor of 2^N. Thus we can now write the partition function in the absence of a magnetic field in the form

$$Z_N{}^I = 2^N(\cosh K)^{\mathscr{N}}\left[1+\sum_{r=1}^{\mathscr{N}} p(r)\tanh^r K\right] \quad . \quad . \quad . \quad (34)$$

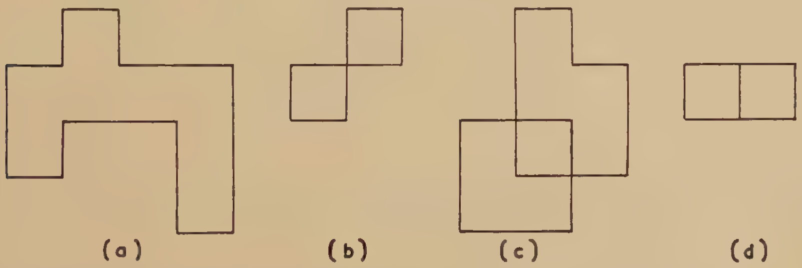
where $p(r)$ is the number of independent polygons defined above which can be constructed with r nearest neighbour links in the lattice.

The expansion (34) can readily be generalized to the case of asymmetric interactions in different directions in the lattice. Thus for an S.Q. lattice with a horizontal interaction J and a vertical interaction J' and n horizontal and m vertical nearest neighbour links it is easy to show that

$$Z_N{}^I = 2^N[\cosh K]^{\mathsf{n}}[\cosh K']^{\mathsf{m}}\left[1+\sum_{r=1}^{\mathsf{n}}\sum_{s=1}^{\mathsf{m}} p(r,s)\tanh^r K\tanh^s K'\right] \quad . \quad . \quad . \quad (35)$$

where $p(r,s)$ is the number of polygons with r horizontal and s vertical links.

Fig. 7



Typical polygons in the zero field expansion. (*a*), (*b*), (*c*) contribute ; (*d*) does not contribute.

Finally in terms of our previously defined functions and variables the relations (34), (35) can be written,

$$\left.\begin{aligned} \Lambda_N(1,z) &= 2^N\left(\frac{1+z}{2}\right)^{qN/2}\left[1+\sum_r p(r)v^r\right], \quad v=(1-z)/(1+z), \\ \Lambda_N(1\,;\ z,z') &= \left[\frac{(1+z)(1+z')}{2}\right]^N\left[1+\sum_{r,s} p(r,s)v^r v'^s\right], \end{aligned}\right\} \quad (36)$$

the second relation applying to a quadratic lattice with equal numbers of horizontal and vertical links.

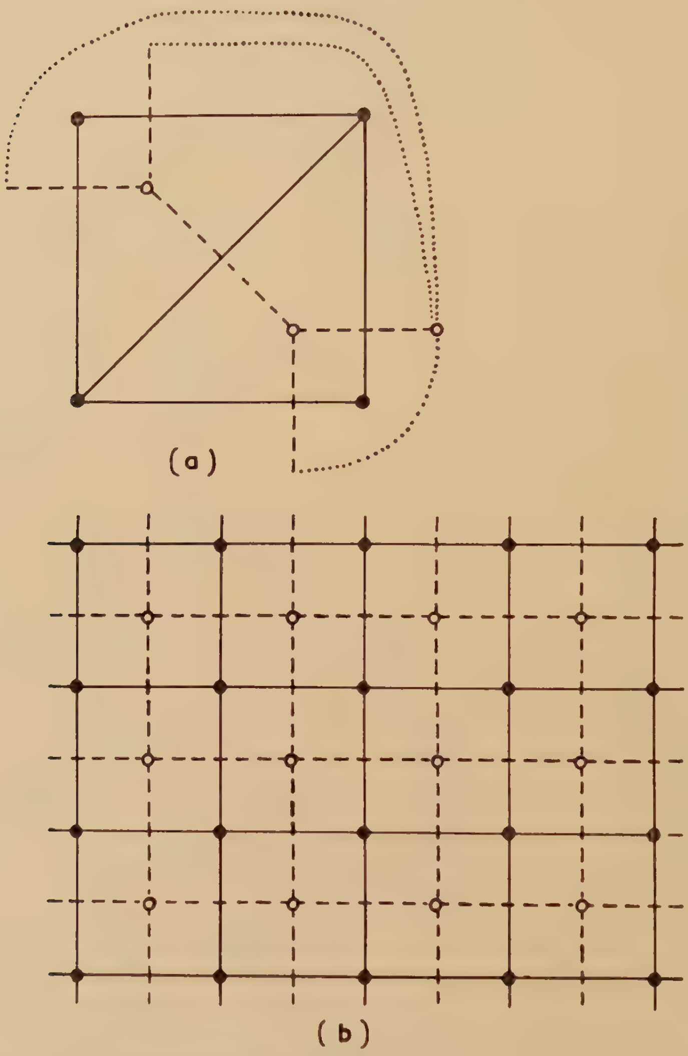
3.4.2. *The duality transformation in two-dimensional nets*

Using a unitary transformation on the matrices discussed in § 3.2.2 for the two-dimensional quadratic lattice, Kramers and Wannier (1941) established the relationship:

$$\Lambda(1,z) = \frac{2}{(1+v)^2}\Lambda(1,v), \quad \left[v=\frac{(1-z)}{(1+z)}\right]. \quad . \quad . \quad . \quad (37)$$

They were thus able to establish a 1–1 correspondence between the partition function for a value z, and the partition function for a value $v=(1-z)/(1+z)$. As $T\to 0$, $z\to 0$ and $v\to 1$, and vice versa; knowing the partition function at low temperatures from $z=0$ to $z=z_c=(\sqrt{2}-1)=(1-z_c)/(1+z_c)$ the values from $z=z_c$ to $z=1$ could automatically be deduced. Kramers and Wannier thus concluded that if any singularity occurred for $z<z_c$ it would be repeated for $z>z_c$, and if there was only one singularity it must occur at $z=z_c$. Hence they conjectured that the Curie point of the quadratic lattice occurred at $z=z_c=(\sqrt{2}-1)$. By evaluating the specific heat at this point for finite matrices of increasing magnitude, Kramers and

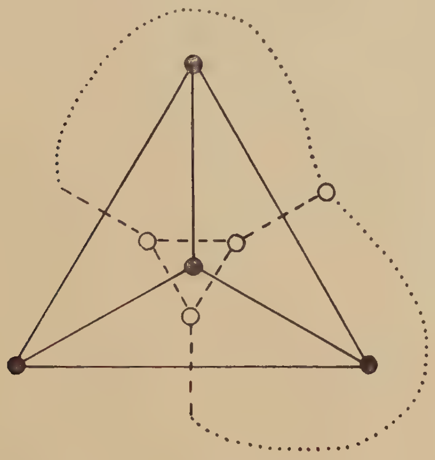
Fig. 8



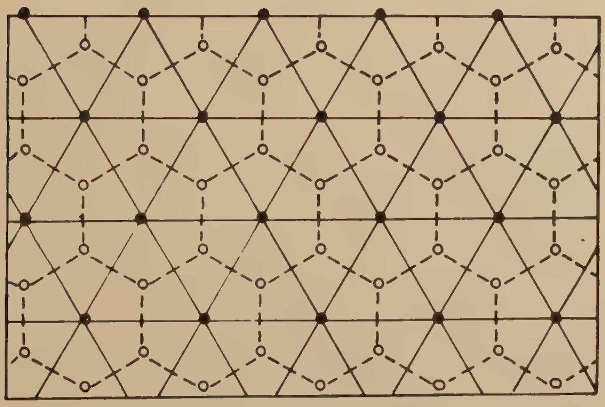
Wannier also conjectured that the specific heat was infinite at the Curie point.

A topological interpretation of this transformation was given by Onsager (see Wannier 1945) which gives a clearer understanding of its nature, and enables its application to be extended considerably. For any two-dimensional net we define a dual net by placing spins into every elementary polygon and drawing lines of interaction between them so that each old line is crossed by a new one. The duality relation is clearly a reciprocal one; the number of polygons in one net equals the number of vertices in the other, while the number of sides is the same. Examples of two-dimensional nets and their duals are given in fig. 8, and have been taken from Wannier's paper (1945). In cases (*b*) and (*c*) the dual net is

Fig. 8 (*continued*)



(*c*)



(*d*)

Two dimensional nets and their duals (after Wannier).

topologically identical with the original; such nets may be referred to as 'self dual'.

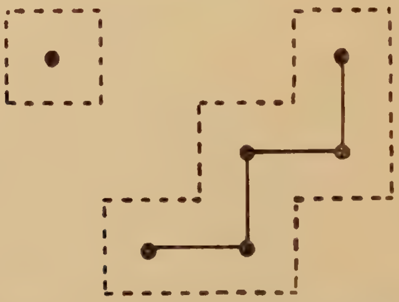
For any Ising net it was pointed out in § 3.4.1 that the partition function can be expanded as a series of terms, each corresponding to more overturned spins and hence more deviations from the ground state. Thus for an Ising net of N spins and $\mathcal{N}$ links in the absence of a magnetic field, we may write

$$Z_N = 2\exp(\mathcal{N}J/kT)\left[1+\sum_{r=1}^{r_{\max}} \nu(r)\exp-(2rJ/kT)\right]\dagger \quad . \quad (38)$$

The factor 2 arises because of the degeneracy of the lowest energy state and $\nu(r)$ is the number of configurations corresponding to r broken links. It is not difficult to see that the number of configurations $\nu(r)$ with r broken links in a given lattice is equal to the number of closed polygons $p(r)$ of the type defined in § 3.4.1 for the dual lattice (see fig. 9). Thus if we use an asterisk to denote parameters of the dual lattice $\nu(r)=p^*(r)$. From (34) we have

$$Z_N{}^* = 2^{N^*}(\cosh K^*)^{\mathcal{N}^*}\left[1+\sum_{r=1}^{\mathcal{N}^*} p^*(r)\tanh^r K^*\right]. \quad . \quad . \quad (39)$$

Fig. 9



Equality of broken links on original lattice with polygons on dual lattice.

Hence if we relate K^* to K so that

$$\tanh K^* = \exp(-2K) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

we obtain

$$\frac{Z_N{}^*(K^*)}{2^{N^*}(\cosh K^*)^{\mathcal{N}^*}} = \frac{Z_N(K)}{2\exp(\mathcal{N}K)}. \quad . \quad . \quad . \quad . \quad (41)$$

Using the topological relations $\mathcal{N}=\mathcal{N}^*$, $N+N^*=\mathcal{N}+2$, (41) can be put in the more symmetrical form

$$\frac{Z_N(K)}{2^{N/2}(\cosh 2K)^{\mathcal{N}/2}} = \frac{Z_N{}^*(K^*)}{2^{N^*/2}(\cosh 2K^*)^{\mathcal{N}/2}}. \quad . \quad . \quad . \quad (42)$$

The relation (42) means that if we know the partition function of any net we can immediately write down the corresponding partition function

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† We shall drop the superscript I in Z_N when this does not lead to confusion.

for the dual net. The relation (40) may be put more symmetrically in the form

$$\sinh 2K^* \sinh 2K = 1, \qquad \ldots\ldots \quad (43)$$

or in terms of z variables

$$z^* = v = (1-z)/(1+z); \quad (1+z)(1+v) = 2\dagger. \qquad \ldots \quad (44)$$

The transformation (37) is derived from (42) when the dual net is identical with the original net (with the exception of end effects) and this is the case for a quadratic net (fig. 8 *b*). We find that

$$Z_N{}^*(K^*) = \frac{2^{N/2}}{2^{N^*/2}}\left(\frac{\cosh 2K^*}{\cosh 2K}\right)^{\mathcal{N}/2} Z_N(K) \qquad \ldots \quad (45)$$

and (37) follows readily ($N^* \simeq N \simeq \mathcal{N}/2$) on taking the Nth root and substituting from (44).

When a quadratic lattice is wrapped on a torus the relation $\nu(r) = p^*(r)$ is satisfied only for configurations which do not loop the torus (or loop it an even number of times); the duality relation is, therefore, not satisfied exactly.

The duality relation (42) can be established equally well for asymmetric nets using (35). Corresponding to (44) we will now have relations

$$v = (1-z')/(1+z'), \quad v' = (1-z)/(1+z), \qquad \ldots\ldots \quad (46)$$

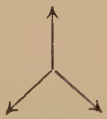
and instead of (37) we find

$$\Lambda(1;\ z, z') = \frac{2}{(1+v)(1+v')}\Lambda(1;\ v', v). \qquad \ldots \quad (47)$$

The relation (46) can no longer be solved for a given set of interaction constants to provide a unique relationship between T^* and T. However, if we interpret the transformation from z to v variables as converting order into disorder the Curie points correspond to the meeting points of the ordered and disordered regions in the (z, z') plane; they will therefore be determined by

$$\left.\begin{array}{c} z = (1-z')/(1+z'), \quad z' = (1-z)/(1+z), \\ \text{or} \\ (1+z)(1+z') = 2 \end{array}\right\} \qquad \ldots \quad (48)$$

Using methods similar to Kramers and Wannier, Potts (1952) established an inversion transformation for a generalized interaction allowing more than two configurations for an individual spin. If the spins are allowed three configurations each 120° to one another,



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†The variable v will be used for the inversion transformation § 3.4.3. For the quadratic lattice the duality and inversion transformations are identical.

and $-J_0$ is the interaction between parallel spins and $-J_1$ between spins oriented at 120° to each other, the Curie point is given by

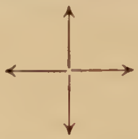
$$z=\exp\left[-(J_0-J_1)/kT_c\right]=(1+\sqrt{3})^{-1}. \quad . \quad . \quad . \quad (49)$$

This is a special case of a more general problem in which r kinds of units in equal abundance form a square lattice, and nearest neighbours interact with only two possible energies, $-J_0$ for like units, and $-J_1$ for unlike units. For the general problem the Curie point is given by

$$z_c=\exp\left[-(J_0-J_1)/kT_c\right]=(1+\sqrt{r})^{-1}. \quad . \quad . \quad . \quad (50)$$

The particular case $r=4$ had been previously considered by Ashkin and Teller (1943).

If the spins are allowed four configurations at right angles to one another



and $-J$ is the interaction energy of parallel spins, $+J$ of anti-parallel spins, and zero of perpendicular spins, the Curie temperature T_c is given by

$$z_c=\exp(-2J/kT_c)=(3+2\sqrt{2})^{-1}, \quad . \quad . \quad . \quad . \quad (51)$$

and is exactly half of the Curie temperature for the simple Ising model.

These particular models do not correspond exactly to an Ising interaction with a higher value of spin. However, since the duality transformation can be applied to them, it is rather likely that an exact solution can be found in closed form (as for the Ising model), and they might, therefore, provide a useful indication of the effect of a change in the type of interaction on the thermodynamic properties of the model.

3.4.3. *The star-triangle transformation*

The dual of a triangular lattice is a honeycomb lattice (fig. 8), and hence the relation (42) cannot be used directly to determine its Curie point. However, Onsager made use of the ' star-triangle ' transformation to relate the partition functions for the triangular and honeycomb lattices, and hence to determine the Curie points of both. The star-triangle transformation replaces a star consisting of three spins interacting with a central spin, by a triangle of spins interacting with one another (see fig. 10); it can readily be established by using the relation (32).

Let us consider the simplest case in which all the interactions are equal. Then summing over σ_0 in the partition function for the star, we obtain

$$\sum_{\sigma_0=\pm1}\exp K(\sigma_0\sigma_1+\sigma_0\sigma_2+\sigma_0\sigma_3)=$$

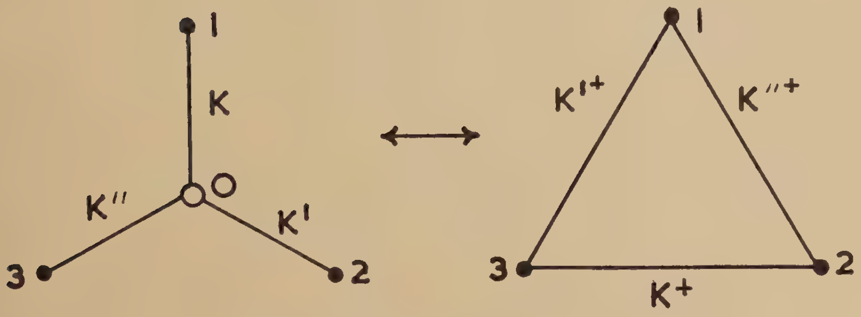
$$\sum_{\sigma_0=\pm1}\cosh^3 K(1+\sigma_0\sigma_1\tanh K)(1+\sigma_0\sigma_2\tanh K)(1+\sigma_0\sigma_3\tanh K)$$

$$=2\cosh^3 K+2\sinh^2 K\cosh K(\sigma_1\sigma_2+\sigma_2\sigma_3+\sigma_3\sigma_1). \qquad (52)$$

However, the partition function for a triangle of spins with interaction K^+ is given by

$$\begin{aligned}\exp K^+(\sigma_1\sigma_2+\sigma_2\sigma_3+\sigma_3\sigma_1) &= \cosh^3 K^+(1+\sigma_1\sigma_2\tanh K^+)(1+\sigma_2\sigma_3\tanh K^+)(1+\sigma_3\sigma_1\tanh K^+)\\ &= (\cosh^3 K^+ + \sinh^3 K^+) + (\cosh^2 K^+ \sinh K^+ + \cosh K^+ \sinh^2 K^+)\\ &\qquad \times (\sigma_1\sigma_2+\sigma_2\sigma_3+\sigma_3\sigma_1). \quad . \quad . \quad . \quad (53)\end{aligned}$$

Fig. 10



The star-triangle transformation.

Comparing (52) and (53), we see that if we chose K^+ to satisfy

$$\frac{\cosh K^+ \sinh K^+ (\cosh K^+ + \sinh K^+)}{(\cosh^3 K^+ + \sinh^3 K^+)} = \tanh^2 K \quad . \quad . \quad (54)$$

the interactions of the star and triangle will be related to each other by the simple factor

$$f = 2\cosh^3 K/(\cosh^3 K^+ + \sinh^3 K^+).$$

If we now apply the star-triangle transformation to the lattice points represented by open circles in (fig. 11), we easily deduce that

$$Z_{2N}{}^H(K) = f^N Z_N{}^T(K^+) \quad . \quad . \quad . \quad . \quad . \quad . \quad (55)$$

where the superscripts H and T refer to the honeycomb and triangular lattices.

Now from (42) we have the duality relationship

$$\frac{Z_N{}^T(K^*)}{2^{N/2}(\cosh 2K^*)^{3N/2}} = \frac{Z_{2N}{}^H(K)}{2^N(\cosh 2K)^{3N/2}}. \quad . \quad . \quad . \quad . \quad (56)$$

Combining (55) and (56) we obtain a relation between $Z_N{}^T(K^*)$ and $Z_N{}^T(K^+)$, to which the argument of the previous section can be applied. The relation (54) between the variables can be more simply expressed as

$$\left.\begin{aligned}\exp 4K^+ &= 2\cosh 2K - 1,\\ z^{+2} &= 3/(1-z+z^2),\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (57)$$

and hence from (44) the reciprocal relation between z^+ and z^* is

$$\left.\begin{aligned} z^{+2}&=(1-z^{*2})/(1+3z^{*2}),\\ [\exp(4K^+)-1][\exp(4K^*)-1]&=4.\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (58)$$

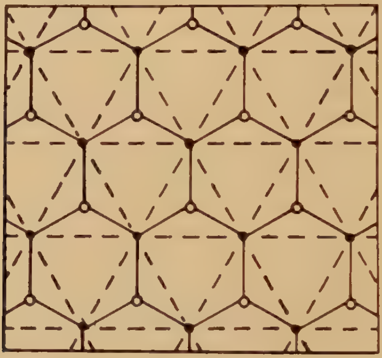
Following Wannier (1950) we shall refer to the transformation between variables such as z^* and z^+ as an 'inversion' transformation. For the quadratic lattice the duality transformation is thus identical with the inversion transformation. Using (43) and (45) it can be put in the alternative form

$$\frac{Z_N(K)}{(2\sinh 2K)^{N/2}}=\frac{Z_N(K^*)}{(2\sinh 2K^*)^{N/2}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (59)$$

The Curie point of the triangular net is given by $z^*=z^+$, or

$$(1+z_c{}^2)(1-3z_c{}^2)=0, \quad z_c=1/\sqrt{3}.$$

Fig. 11



The honeycomb lattice. Application of the star-triangle transformation to the spins represented by open circles and their three neighbours leads to the triangular lattice (broken lines).

The inversion transformation for the triangular lattice follows from (55) and (56); Wannier noted that this transformation was of exactly the same form as (59) in the variables K^+ and K^*. The form corresponding to (37) is

$$\Lambda(1,z)=\frac{2}{1+3v^2}\Lambda(1,v), \quad v^2=(1-z^2)/(1+3z^2) \quad . \quad . \quad . \quad (60)$$

and this form is useful in the derivation of series expansions.

For the honeycomb lattice the corresponding relationship from (55) and (56) is between $Z_{2N}{}^H(K)$ and $Z_{2N}{}^H(K^{+*})$ where $z^{+*}=(1-z^+)/(1+z^+)$. The Curie point is given by $z=z^{+*}$ so that $(1+z_c{}^2)(1-4z_c+z_c{}^2)=0$, $z_c=2-\sqrt{3}$. The relation between z and z^{+*} is

$$\left.\begin{aligned} z^{+*}&=\frac{\sqrt{(1-z+z^2)}-\sqrt{z}}{\sqrt{(1-z+z^2)}+\sqrt{z}},\\ (\cosh 2K^{+*}-1)(\cosh 2K-1)&=1.\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (61)$$

Again the relation (59) is valid in the variables K and K^{+*}, and the transformation can be written

$$\left.\begin{aligned} \Lambda(1,z) &= 2[1+v^3]^{-1/2}\left[1+\sqrt{\left(\frac{v}{1-v+v^2}\right)}\right]^{-3/2}\Lambda(1,v), \\ v &= \frac{\sqrt{(1-z+z^2)}-\sqrt{z}}{\sqrt{(1-z+z^2)}+\sqrt{z}}. \end{aligned}\right\} \quad . \quad (62)$$

It will be noted that the equations determining the Curie points of the quadratic and honeycomb lattices have identical solutions for z and z^{-1}, whereas the triangular lattice has only the one solution $z_c = 1/\sqrt{3}$. This corresponds to the fact that perfectly ordered antiferromagnetic arrangements exist for the first two lattices but not for the third (§ 3.5.4).

Duality transformations can be derived in a similar manner when the interactions are different for different directions in the lattice. The detailed calculations are somewhat complicated by the methods of this section, and follow more readily from the general approach of Fisher to be described in (§ 3.4.5). We shall quote the results for reference (Houtappel 1950, Potts 1951).

For a triangular lattice with ferromagnetic interactions J, J', J'' the Curie point is given by

$$zz' + zz'' + z'z'' = 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (63)$$

When one of the interactions becomes zero we recover the formula (44) for a rectangular lattice. More generally when interactions can be ferromagnetic or antiferromagnetic the equation determining the Curie point is

$$\sinh 2K \sinh 2K' + \sinh 2K' \sinh 2K'' + \sinh 2K'' \sinh 2K = 1. \qquad (64)$$

This equation is valid when the largest two of J, J', J'' are positive, i.e. $J+J' > 0$, $J'+J'' > 0$, $J''+J > 0$. Other cases can be dealt with since any two of J, J', J'' can change sign without affecting the Curie point, and (64) can then be used for the new values if they satisfy the condition of validity. There is no Curie point if and only if one or three of the J's are negative and the two weakest J's are exactly equal; in these cases no ordered lowest energy state occurs.

For the honeycomb lattice with different interactions in different directions the corresponding equation is

$$\sinh 2|K| + \sinh 2|K'| + \sinh 2|K''| = \sinh 2|K| \sinh 2|K'| \sinh 2|K''|. \quad . \quad . \quad (65)$$

This lattice always has a Curie point for any values of J, J', J''.

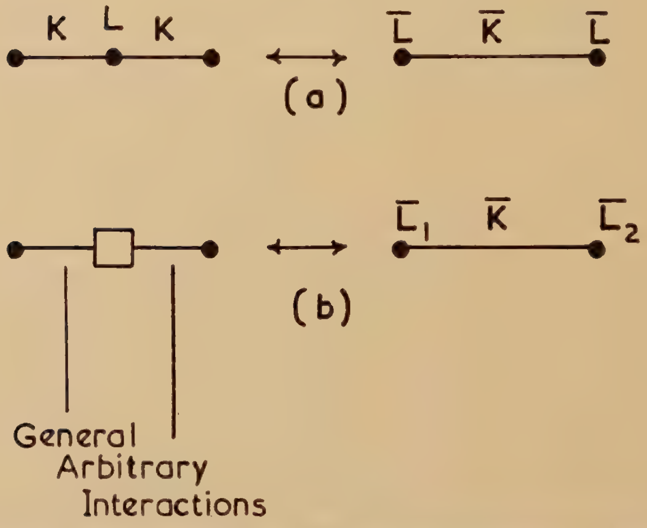
3.4.4. *The decoration transformation*

A transformation similar to the star-triangle transformation was suggested by Syozi (1951) and developed by Naya (1954). This applies to a single central spin connected to two spins, and replaces them (including the interaction with an external magnetic field) by an interaction along a single bond between the two atoms, and a change in magnetic field interaction of these atoms (see fig. 12 *a*); the central spin will be referred to as a decorating spin.

Taking the simple case shown in fig. 12 *a*, and summing over σ_0 in the partition function for the three spins we obtain

$$\begin{aligned}\sum_{\sigma_0=\pm1} &\exp(K\sigma_0\sigma_1+K\sigma_0\sigma_2+L\sigma_0), \quad (L=mH/kT)\\ &=\sum_{\sigma_0=\pm1}(\cosh K+\sigma_0\sigma_1\sinh K)(\cosh K+\sigma_0\sigma_2\sinh K)\\ &\quad\times(\cosh L+\sigma_0\sinh L)\\ &=2\cosh^2 K\cosh L+2\sigma_1\sigma_2\sinh^2 K\cosh L+2(\sigma_1+\sigma_2)\\ &\quad\times\cosh K\sinh K\sinh L. \qquad \text{. . . . (66)}\end{aligned}$$

Fig. 12



The decoration transformation. (*a*) Simple transformation for atoms of spin 1/2; (*b*) Central spin replaced by an arbitrary interacting system.

But the partition function for a pair of spins with interaction $\bar{K}$ and magnetic interaction $\bar{L}$ is given by

$$\begin{aligned}\exp(\bar{K}\sigma_1\sigma_2+\bar{L}\sigma_1+\bar{L}\sigma_2)&=(\cosh\bar{K}+\sigma_1\sigma_2\sinh\bar{K})(\cosh\bar{L}+\sigma_1\sinh\bar{L})\\ &\quad\times(\cosh\bar{L}+\sigma_2\sinh\bar{L})\\ &=\cosh\bar{K}\cosh^2\bar{L}+\sigma_1\sigma_2[\cosh^2\bar{K}\sinh\bar{L}+\sinh^2\bar{K}\cosh\bar{L}]\\ &\quad+(\sigma_1+\sigma_2)(\cosh\bar{K}+\sinh\bar{K})\cosh\bar{L}\sinh\bar{L}. \qquad \text{. . . . . (67)}\end{aligned}$$

Hence $\bar{K}$ and $\bar{L}$ can be chosen so that the two expressions (66) and (67) are equivalent except for a simple factor. The appropriate values of $\bar{K}$ and $\bar{L}$ satisfy.

$$\left.\begin{aligned}\tanh^2 K&=\tanh\bar{K}+\tanh^2\bar{L},\\ \tanh K\tanh L&=\tanh\bar{L}+\tanh\bar{K}\tanh\bar{L}.\end{aligned}\right\} \qquad \text{. . (68)}$$

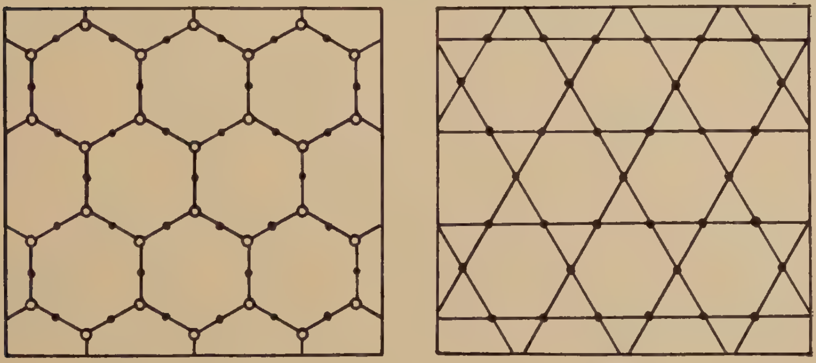
Using this transformation Naya derived a relation between the partition functions for the magnetic honeycomb lattice with parameters $\bar{K}$, $\bar{L}$, and the decorated honeycomb lattice with parameters K, L as shown in fig. 13. (In the decorated lattice spins represented by open circles are non-magnetic and do not interact with an external field.) The star-triangle transformation was now used to remove the non-magnetic spins and the kagomé lattice (fig. 13 *b*) was derived. He thus obtained a relation between the partition functions of the honeycomb and kagomé lattices in the presence of a magnetic field. The relation may be symbolically characterized as follows:

$$Z_N{}^H(\bar{K},\bar{L}) \rightarrow Z_{2N}{}^{\mathrm{Dec}}(K,L) \rightarrow Z_N{}^K(K^+,L). \quad . \quad . \quad . \qquad (69)$$

The relation (69) can be used to derive the Curie point of the kagomé lattice. Taking $\bar{L}=0$ we find from (68) that $L=0$, and the relation between $\bar{K}$ and K reduces to

$$\tanh \bar{K} = \tanh^2 K. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (70)$$

Fig. 13


(*a*) (*b*)

The decorated honeycomb lattice and the kagomé lattice. Application of the star-triangle transformation to the spins represented by open circles (*a*) yields the kagomé lattice, (*b*).

Using the relation (49) between z and z^+, we find for z^+ and $\bar{z}$

$$z^{+2} = \bar{z}/(2-\bar{z}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (71)$$

and since the Curie point of the honeycomb lattice is given by $\bar{z}_c = 2-\sqrt{3}$, the Curie point of the kagomé lattice is given by

$$z_c{}^+ = \left(\frac{2}{\sqrt{3}} - 1\right)^{1/2}$$

(Syozi 1951).

The kagomé lattice has coordination number 4, and all points and bonds are equivalent, but its Curie temperature is lower than that of the quadratic lattice.

3.4.5. *Generalized transformations*

Recently Fisher (1959 a) has put forward an alternative approach to the decoration and star triangle transformations which appreciably simplifies the algebraic manipulations, and enables the transformations to be generalized considerably. Let us first consider the decoration transformation but replacing the decorating spin by any arbitrary system interacting with the lattice spins (fig. 12 *b*). The energy levels of this system can then be written in the form $E_i(\sigma_1, \sigma_2; H)$, and the partition function (summing over the decorating system) by

$$\psi(\sigma_1, \sigma_2; H) = \sum_i \exp[-E_i(\sigma_1, \sigma_2; H)/kT]. \quad . \quad . \quad . \quad (72)$$

This is a function of the spin variables σ_1, σ_2 taking on four values corresponding to the four possible combinations $(+,+)(+,-)(-,+)(-,-)$. We wish to replace this function by an interaction along the original bond $\bar{K}$, together with a change in the magnetic interactions of the lattice spins $\bar{L}_1$, $\bar{L}_2$, i.e. by

$$f \exp(\bar{K}\sigma_1\sigma_2 + \bar{L}_1\sigma_1 + \bar{L}_2\sigma_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (73)$$

where f is a factor independent of the spin variables. There are four free variables in (73) and four independent conditions to be satisfied in equating to (72). In fact it is easy to see that they will be satisfied by taking

$$\left.\begin{aligned} \exp(4\bar{L}_1) &= \frac{\psi_{++}\psi_{+-}}{\psi_{--}\psi_{-+}}, \quad \exp(4\bar{L}_2) = \frac{\psi_{++}\psi_{-+}}{\psi_{--}\psi_{+-}}, \\ \exp(4\bar{K}) &= \frac{\psi_{++}\psi_{--}}{\psi_{+-}\psi_{-+}}, \\ f^4 &= \psi_{++}\psi_{--}\psi_{+-}\psi_{-+}, \end{aligned}\right\} \quad . \quad (74)$$

where $\psi_{++} = \psi(+1, +1; H)$ and so on. The example discussed in the previous section is a special case, and $\bar{K}$ and $\bar{L}$ are explicitly determined by (74),

$$\left.\begin{aligned} \exp(4\bar{K}) &= \frac{\cosh(2K+L)\cosh(2K-L)}{\cosh^2 L}, \\ \exp(4\bar{L}) &= \cosh(2K+L)\cosh(2K-L), \\ f^4 &= \cosh(2K+L)\cosh(2K-L)\cosh^2 L. \end{aligned}\right\} \quad (75)$$

But corresponding formulae could readily be written down for different decorating systems, e.g. a spin of magnitude s, or a group of spins.

The partition function for a decorated lattice is reduced to a summation over the original undecorated lattice

$$Z^{\mathrm{D}}(K, L) = f^{\mathcal{N}_{\mathrm{D}}} Z(\bar{K}, \bar{L}), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (76)$$

where $\mathcal{N}_{\mathrm{D}}$ is the number of decorated bonds. It may be noted that the factor f is effectively the partition function of the decorating system averaged over all possible states of the basic lattice spins to which it is coupled. Consequently it will only give rise to critical behaviour if the individual decorating systems exhibit critical behaviour; otherwise the singularities of the decorated lattice will be simply related to the singularities of the original lattice.

Using the same approach towards the star-triangle transformation, and replacing the central spin by an arbitrary interacting system, we must consider the energy levels $E_i(\sigma_1, \sigma_2, \sigma_3;\ H)$. In general there are not enough free parameters in the partition function for the triangle to enable us to establish an identity valid for all σ_1, σ_2, σ_3. However, if we restrict the central interacting system so that the partition function

$$\psi(\sigma_1, \sigma_2, \sigma_3) = \sum_i \exp\left[-E_i(\sigma_1, \sigma_2, \sigma_3)/kT\right] \quad . \quad . \quad . \quad (77)$$

is invariant under the operation of total spin inversion

$$\sigma_1 \to -\sigma_1,\ \ \sigma_2 \to -\sigma_2,\ \ \sigma_3 \to -\sigma_3,$$

we can establish such an identity. Writing

$$\left.\begin{aligned} \psi(+,+,+) &= \psi(-,-,-) = \psi_0, \\ \psi(-,+,+) &= \psi(+,-,-) = \psi_1, \\ \psi(+,-,+) &= \psi(-,+,-) = \psi_2, \\ \psi(+,+,-) &= \psi(-,-,+) = \psi_3, \end{aligned}\right\} \quad . \quad . \quad . \quad (78)$$

we must equate (77) with the partition function for a triangle of spins

$$f \exp\left(K_1^+\sigma_2\sigma_3 + K_2^+\sigma_3\sigma_1 + K_3^+\sigma_1\sigma_2\right). \quad . \quad . \quad . \quad . \quad (79)$$

This can be satisfied identically if we take

$$\left.\begin{aligned} &\exp(4K_1^+) = \psi_0 \frac{\psi_1}{\psi_2\psi_3}, \quad \exp(4K_2^+) = \psi_0 \frac{\psi_2}{\psi_3\psi_1}, \\ &\exp(4K_3^+) = \psi_0 \frac{\psi_3}{\psi_1\psi_2}, \qquad\qquad f^4 = \psi_0\psi_1\psi_2\psi_3. \end{aligned}\right\} \quad . \quad . \quad (80)$$

Again the partition function of a 'starred' lattice is related to the partition function of the basic 'triangle' lattice by

$$Z^{\mathrm{S}}(K_1, K_2, K_3) = f^{N_{\mathrm{S}}} Z(K_1^+, K_2^+, K_3^+),$$

where N_{S} is the number of star vertices.

The restriction of invariance in the central interacting system means that there is no preferred direction for this system, and effectively restricts the spins of this system to having no magnetic moment. As an example of the application of (80) we can write down the general form of the star-triangle transformation for a single central spin with different interactions in different directions discussed at the end of § 3.4.3:

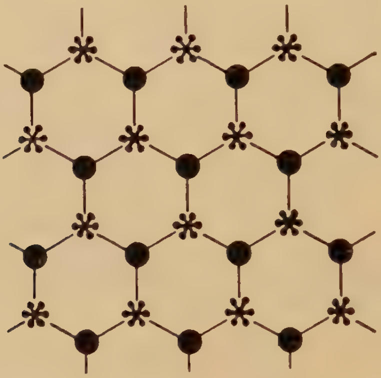
$$\left.\begin{aligned} \exp(4K^+) &= \frac{\cosh(K+K'+K'')\cosh(-K+K'+K'')}{\cosh(K-K'+K'')\cosh(K+K'-K'')}, \\ \exp(4K'^+) &= \frac{\cosh(K+K'+K'')\cosh(K-K'+K'')}{\cosh(-K+K'+K'')\cosh(K+K'-K'')}, \\ \exp(4K''^+) &= \frac{\cosh(K+K'+K'')\cosh(K+K'-K'')}{\cosh(-K+K'+K'')\cosh(K-K'+K'')}, \\ f^4 = 2^4 &\cosh(K+K'+K'')\cosh(-K+K'+K'', \\ &\cosh(K-K'+K'')\cosh(K+K'-K''). \end{aligned}\right\} \quad . \quad (81)$$

Similarly for a central spin of magnitude s interacting with three standard spins of magnitude $\frac{1}{2}$ the transformation energy parameter is given by

$$\exp(4K^{+}) = \{1 + 2\cosh[(2s+1)K/s]\}/[1 + 2\cosh(K/s)] \quad . \quad . \quad (82)$$

where the interaction energy between the central and outer spins is normalized so that its maximum and minimum values are $\pm J (K = J/kT)$. By this means we can relate the partition function of the alternate honeycomb lattice (fig. 14) to that of the triangular lattice.

Fig. 14



Honeycomb lattice half the spins having $s = 1/2$, and the other half having arbitrary s.

3.5. *Exact Solutions for Two-dimensional Ising Models*

The most important landmark in the field of cooperative phenomena was the exact solution in 1944 by Onsager of the two-dimensional Ising model in the absence of a magnetic field. Onsager's method involved the theory of group representations, and a substantial knowledge of algebra is required to follow the detailed work. A few years later Kaufman (1949) substantially simplified the development by the use of spinor analysis, and Kaufman and Onsager (1949) showed how the degree of order could be calculated between any two lattice sites. In 1952 Kac and Ward introduced a more elementary approach to the problem, which can be understood without detailed algebraic knowledge; they were able to reproduce all the results which had been derived previously. It is not our intention to provide the mathematical details of the various derivations, since they are clearly set out in the original papers, and have been further discussed in a review paper (Newell and Montroll 1953). However, we shall endeavour to summarize briefly the various methods of approach, and to reproduce fully the conclusions regarding the mathematical and physical properties of the resulting solution.

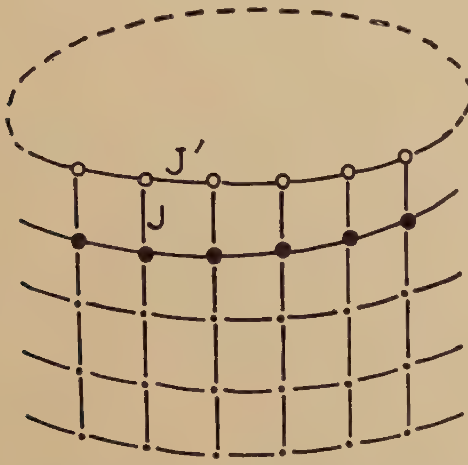
3.5.1. *Onsager's solution*

Onsager considered a two dimensional lattice each layer of which contained spins connected to form a circle (fig. 15). The theory of § 3.2 applies, and since successive layers are connected to form a ring, the complete lattice is wrapped on a torus. The interaction $U(\sigma, \sigma^+)$ between successive layers, which gives rise to a matrix $\mathbf{V}$ of order 2^n, can be divided into two parts, a portion between successive layers, and a portion within the added layer. It can be written symbolically as

$$U(\sigma, \sigma^+) = -J \sum_{i=1}^{n} \sigma_i \sigma_i^+ - J' \sum_{i=1}^{n} \sigma_i \sigma_{i+1} \quad (\sigma_{i+n} \equiv \sigma_i), \quad . \quad . \quad (83)$$

where the σ_i are variables which can take the values ± 1, as in § 3.3.

Fig. 15



Each added layer consists of a circle of n spins. The added interaction can be divided into two parts (i) a portion between the final two layers ● and ○, (ii) a portion within the final layer ○.

Correspondingly $\mathbf{V}$ can be written as a product

$$\mathbf{V} = \prod_{i=1}^{n} \exp K(\sigma_i \sigma_i^+) \prod_{i=1}^{n} \exp K'(\sigma_i \sigma_{i+1}). \quad . \quad . \quad . \quad (84)$$

The $\exp K(\sigma_i \sigma_i^+)$ can be expressed in terms of operators with simple properties. When only one particular i is considered $\exp K(\sigma_i \sigma_i^+)$ can be represented by a 2×2 matrix.

$$\begin{pmatrix} e^{K} & e^{-K} \\ e^{-K} & e^{K} \end{pmatrix} = e^{K} I + e^{-K} \mathbf{C}_i \quad \left[\mathbf{C}_i = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \right]. \quad . \quad . \quad (85)$$

The operator $\mathbf{C}_i$ changes σ_i into $-\sigma_i$ and satisfies $\mathbf{C}_i^2 = 1$; thus using (43), (85) may be written in the alternative form $(2 \sinh 2K)^{1/2} \exp(K^* \mathbf{C}_i)$. When n independent σ_i enter, each $\mathbf{C}_i$ can be represented by an operator in 2^n dimensional space, and $\mathbf{C}_i$, $\mathbf{C}_j$ commute. If we represent any eigenvector by $|\sigma_1, \ldots, \sigma_i, \ldots \sigma_n\rangle$ we can write

$$\mathbf{C}_i|\sigma_1, \ldots, \sigma_i, \ldots, \sigma_n\rangle = |\sigma_1, \ldots, -\sigma_i, \ldots, \sigma_n\rangle. \quad . \quad . \quad (86)$$

We can define similarly an operator $\mathbf{s}_i$ which does not change the sign of σ_i, so that it is represented by

$$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Corresponding to (86), we have

$$\mathbf{s}_i|\sigma_1, \ldots, \sigma_i, \ldots, \sigma_n\rangle = \sigma_i|\sigma_1, \ldots, \sigma_i, \ldots, \sigma_n\rangle. \quad . \quad . \quad . \quad (87)$$

In terms of the operators $\mathbf{C}_i$, $\mathbf{s}_i$, $\mathbf{V}$ can be written in the form

$$(2 \sinh 2K)^{n/2}\mathbf{V}_1\mathbf{V}_2,$$

where

$$\left.\begin{aligned} \mathbf{V}_1 &= \prod_{i=1}^{n} \exp(K^*\mathbf{C}_i), \\ \mathbf{V}_2 &= \prod_{i=1}^{n} \exp(K'\mathbf{s}_i\mathbf{s}_{i+1}). \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (88)$$

Alternatively if we wish to retain the symmetric property we can take $\mathbf{V}$ in the form $(2 \sinh 2K)^{n/2}\mathbf{V}_2^{1/2}\mathbf{V}_1\mathbf{V}_2^{1/2}$. The commutation properties of the $\mathbf{C}_i$, $\mathbf{s}_i$ are as follows:

$$\begin{gathered} \mathbf{s}_i^2 = \mathbf{C}_i^2 = 1, \quad \mathbf{s}_i\mathbf{C}_i = -\mathbf{C}_i\mathbf{s}_i, \\ \mathbf{s}_i\mathbf{s}_j = \mathbf{s}_j\mathbf{s}_i, \quad \mathbf{C}_i\mathbf{C}_j = \mathbf{C}_j\mathbf{C}_i, \quad \mathbf{s}_i\mathbf{C}_j = \mathbf{C}_j\mathbf{s}_i \quad (i \neq j). \quad . \quad . \quad (89) \end{gathered}$$

The set of operators (1, $\mathbf{s}_i$, $\mathbf{C}_i$, $\mathbf{s}_i\mathbf{C}_i$) form a simple quaternion algebra, and hence the algebra of n such sets is a direct product of n simple quaternion algebras.

Defining operators $\mathbf{A}_0$ and $\mathbf{A}_1$ by

$$\left.\begin{aligned} \mathbf{A}_0 &= -\sum_{i=1}^{n} \mathbf{C}_i, \\ \mathbf{A}_1 &= \sum_{i=1}^{n} \mathbf{s}_i\mathbf{s}_{i+1}, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (90)$$

Onsager proceeded to form the commutator $[\mathbf{A}_0\mathbf{A}_1]$, and then the commutators of this with $\mathbf{A}_0$ and $\mathbf{A}_1$; he continued to form commutators of commutators until he obtained a complete set of operators such that the commutator of any two operators is a linear combination of members of the set. Such a set of operators is called a Lie algebra. The Lie algebra generated was of order only $(3n-1)$ and possessed certain characteristic symmetries. Making use of these symmetries Onsager was able to reduce $\mathbf{V}_2\mathbf{V}_1$ to a product of commuting matrices which could be diagonalized separately (for details see Onsager 1944, Newell and Montroll 1953).

If the same procedure is attempted for a two-dimensional lattice in the presence of a magnetic field, or for a three-dimensional lattice, the Lie algebra generated is much larger, and the simplifying features are no longer present. No progress has yet been made in the algebraic approach to these more general problems.

The basic properties of Onsager's solution may be summarized as follows:

(a) *Mathematical properties of the solution*

(i) *The largest eigenvalue* $\lambda_{\max}$ is given by the formula,

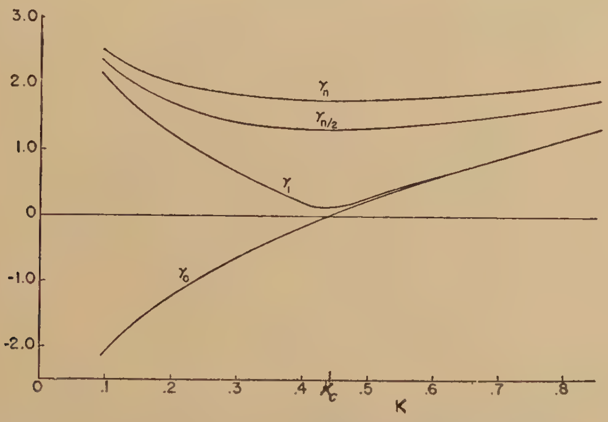
$$\ln \lambda_{\max} - \tfrac{1}{2} n \ln (2 \sinh 2K) = \tfrac{1}{2}(\gamma_1 + \gamma_3 + \ldots + \gamma_{2n-1}). \qquad (91)$$

The γ_r are given by

$$\left.\begin{aligned} \cosh \gamma_r &= \cosh 2K^* \cosh 2K' - \sinh 2K^* \sinh 2K' \cos r\pi/n \\ &= \coth 2K \cosh 2K' - \operatorname{cosech} 2K \sinh 2K' \cos r\pi/n \\ &= \coth 2K \cosh 2K - \cos r\pi/n, \quad (K = K'). \end{aligned}\right\} \qquad (92)$$

It will be seen that the γ_r are invariant under the duality transformation $K' \to K^*$, and hence so is the sum in (91); they are shown graphically in fig. 16 ($K = K'$).

Fig. 16



Dependence of γ_r on temperature (after Kaufman). For $T > T_c (K < K_c)$, $\gamma_1 \simeq -\gamma_0$. For $T < T_c (K > K_c)$, $\gamma_1 \simeq \gamma_0$.

In the limit when the size of the crystal becomes large the series can be replaced by an integral, and the partition function per spin is given by

$$\ln \lambda - \tfrac{1}{2} \ln (2 \sinh K) = \frac{1}{2\pi} \int_0^{\pi} \gamma(\omega)\, d\omega. \qquad (93)$$

This can be transformed into a double integral which is symmetric in K and K' [using the identity

$$\int_0^{2\pi} \ln (2 \cosh x - 2 \cos \omega)\, d\omega = 2\pi x],$$

$$\begin{aligned} \ln (\lambda/2) = \tfrac{1}{2}\pi^{-2} \int_0^{\pi}\!\!\int_0^{\pi} \ln (\cosh 2K \cosh 2K' &- \sinh 2K \cos \omega \\ &- \sinh 2K' \cos \omega')\, d\omega\, d\omega'. \end{aligned} \qquad (94)$$

The various thermodynamic functions can be derived in the standard manner from λ, and many of them are expressible in terms of elliptic integrals; the results are summarized in Appendix II.

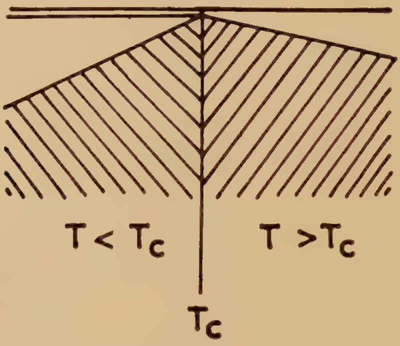
(ii) *The distribution of eigenvalues.* Onsager also obtained the remaining eigenvalues of V, and these enable us to understand the ordering properties of the assembly (§ 3.3.1). The eigenvalues fall into two sets (Kaufman 1949)

$$\left.\begin{aligned} \ln \lambda_i^+ - \tfrac{1}{2} n \ln (2 \sinh 2K) &= \tfrac{1}{2}(\pm \gamma_1 \pm \gamma_3 \cdots \pm \gamma_{2n-1}), \\ \ln \lambda_i^- - \tfrac{1}{2} n \ln (2 \sinh 2K) &= \tfrac{1}{2}(\pm \gamma_2 \pm \gamma_4 \cdots \pm \gamma_{2n}). \end{aligned}\right\} \quad . \quad (95)$$

Here any combination giving an even number of minus signs corresponds to an eigenvalue; there are thus 2^n eigenvalues as expected.

It will be seen from fig. 16 that the γ_r increase steadily from γ_1 to γ_n $(=K'+K^*)$, and for $r>n$ they satisfy the relation $\gamma_r=\gamma_{2n-r}$; for large n they form a closely spaced spectrum between $2|K'-K^*|$ and $2(K'+K^*)$. γ_0 is exceptional, however, since it changes sign at the critical point $K'=K^*$.

Fig. 17



Schematic representation of the distribution of eigenvalues. Shaded portion corresponds to a continuum as $n \to \infty$.

For large n, $\gamma_{2r+1} \simeq \gamma_{2r}$ $(r \neq 0)$ and for $K' > K_c$, i.e. $T < T_c$, $\gamma_1 \simeq \gamma_0$; thus the two sums in (95) are different approximations to $\frac{1}{2}\int_0^{2\pi} \gamma(\omega)\, d\omega$, and the largest eigenvalues λ_1^+ and λ_1^- are very nearly equal. (The difference is exponentially small, all correction terms in the Euler–Maclaurin formula vanishing; see Goodwin 1949.) The next eigenvalue differs from this value by a factor of approximately $\exp 4(K'-K^*)$. However, when $K' < K_c$, i.e. $T > T_c$, $\gamma_1 \simeq -\gamma_0$. Thus the largest eigenvalue λ_1^+ is greater than λ_1^- by a factor of approximately $\exp[2(K^*-K')]$.

We may summarize the distribution of the eigenvalues as follows:

$T<T_c$, $\lambda_1^+=\lambda_1^- >$ continuum of limit $\lambda_1^+ \exp[-4(K'-K^*)]$,

$T=T_c$, $\lambda_1^+=\lambda_1^-=$ limit of continuum,

$T>T_c$, $\lambda_1^+>\lambda_1^-=$ limit of continuum $(\lambda_1^-=\lambda_1^+\exp[-2(K^*-K')])$.

This is illustrated diagramatically in fig. 17.

Following the discussion of order in § 3.3 we see that for $T < T_c$ there is long-range order, arising from the degeneracy of the largest eigenvalue (but this occurs only in the limit as $n \to \infty$). For $T > T_c$ there is no long-range order, and the mean distance to which order persists is given roughly from (26) by the inverse of $\ln(\lambda_1^+/\lambda_1^-)$ or $1/[2(K^* - K')]$.

(iii) *Change in sign of the interaction.* If we replace J' by $-J'$ the interaction becomes antiferromagnetic in one direction; the solution (95) remains valid but a detailed analysis shows a difference between odd and even values of n. We may now write

$$\cosh\gamma_r = \cosh 2K^* \cosh 2K' - \sinh 2K^* \sinh 2K' \cos(\pi - r\pi/n), \qquad (96)$$

so that each γ_r is replaced by γ_{n-r}. When n is even λ_1^+ and λ_1^- are unchanged as we should expect. When n is odd, however, there is a misfit seam; odd γ's are transformed into even γ's, except for $\gamma_n (= K' + K^*)$ which is transformed into $-\gamma_0 (= -K' + K^*)$. Thus λ_1^+ is transformed into λ_1^- with the exception of the change of sign of γ_0. We may, therefore, use the discussion of (ii) to conclude that when $T > T_c$ the partition function is unchanged, but when $T < T_c$ there is an additional factor

$$\exp[-2(K' - K^*)];$$

this will be interpreted as a 'boundary tension'. However, the largest eigenvalue becomes multiply degenerate for $T < T_c$, as we should expect from the degeneracy in position of the misfit seam.

(b) *Physical properties of the solution*

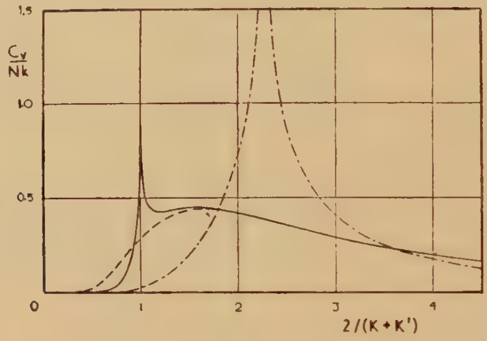
(i) *The specific heat* manifests a striking singularity at the Curie point. It is logarithmically infinite on both sides of the Curie temperature, and is drawn in fig. 18 for the symmetric net. For temperatures near to T_c the following approximation may be used:

$$\left.\begin{aligned} C_V/nmk &\simeq (2/\pi)(\ln\cot\pi/8)^2(K_1 - 1 - \pi/4), \\ K_1 &= \ln(2^{1/2}/|K - K_c|). \end{aligned}\right\} \qquad (97)$$

It should be noted that the specific heat curve differs substantially from any curves which have been observed experimentally, particularly in regard to the magnitude of the 'tail' above the Curie temperature. This can be seen more clearly from the critical value of the entropy, which shows that the entropy change above T_c $(=0{\cdot}387)$ is greater than that below T_c $(=0{\cdot}306)$. It is important to assess whether this is a characteristic of the Ising interaction, or merely dependent upon the two-dimensional character of the model; we shall take this point up again in § 4.7 in discussing the properties of the three-dimensional model. We may incidentally draw attention to a recent remarkable experiment by Fairbank *et al.* (1958) on the anomaly in liquid ^{4}He which has shown clearly that it is logarithmic on both sides of the critical temperature.

For an asymmetric net the logarithmic nature of the specific heat anomaly is unchanged. As one of the interactions J' becomes small the Curie temperature moves to zero, but this movement is very slow; if the interaction J' is J/ν then the reduction in T_c is of order $\ln \nu$ for large ν. The specific heat curve for an asymmetric net in which $J'=J/100$ was calculated by Onsager, and is shown in fig. 18 for comparison with the symmetric net, and with the specific heat of a one dimensional chain ($J'=0$). The abcissa is $2kT/(J+J')$ so that the areas under all the curves are the same. It will be seen that the large asymmetry reduces the Curie point by a factor of 2 only. Also there is an essential difference below the Curie temperature between a two-dimensional net with one small interaction, and a one dimensional chain; as pointed out in § 3.2.1 the latter can be regarded as an assembly whose Curie point has moved to $T=0$.

Fig. 18



Specific heat of a rectangular lattice. – · – · – · – · –$J'=J$ (symmetric) ————$J'=J/100$; – – – – – – – –$J'=0$ (linear chain) (after Onsager).

(ii) *Other thermodynamic quantities.* The internal energy E has a vertical tangent on both sides of the Curie point and is shown in fig. 19 (for the symmetric net). Near the Curie point it is of the form

$$A_0+B_0(T-T_c)\ln|T-T_c|.$$

The free energy F involves an integral of the internal energy and therefore has infinite curvature at the Curie point. The entropy can readily be obtained from the relation $S=(E/T)-F$. Its behaviour at the Curie point is similar to that of the energy. Critical values are given in Appendix II.

(iii) *The boundary tension.* We have seen that when the sign of the interaction energy J' is changed, if n is odd there is a misfit seam which divides regions of opposite order. The partition function (per spin) of such a boundary is

$$\lambda_b'=\exp[-2(K'-K^*)]=z'(1+z)/(1-z). \quad . \quad . \quad . \quad (98)$$

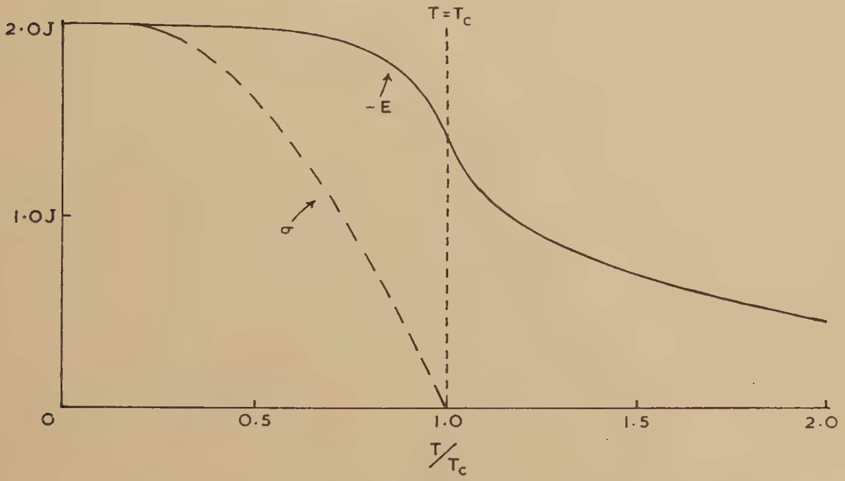
The corresponding boundary free energy is

$$\sigma'=2J'-kT\ln\coth(J/kT);$$

it vanishes at the critical point and is shown in fig. 19 for a symmetric net ($J=J'$). It is thus significant that the critical points are identical for the boundary and for the bulk substance. Corresponding boundary functions λ_b, σ in the perpendicular direction are obtained by interchanging J and J'.

It was pointed out by Onsager and Temperley (Temperley 1952) that the formula (98) is exactly the partition function which would be obtained if only a particular class of boundaries (forward boundaries in the J' direction) were considered. Temperley (1952) attempted to use this result to draw some conclusions about polymer configurations on a quadratic lattice, but Fisher (1958) showed that these considerations are invalid.

Fig. 19



Energy and boundary tension of a quadratic lattice.
———— E has infinite slope at T_c ; ·········· σ is zero for $T \geqslant T_c$.

(iv) *The specific heat of a finite crystal.* The specific heat of a finite crystal of n rows can be computed from eqn. (91). It is finite at all temperatures, since the partition function is an analytic function of the temperature, but a maximum occurs near the transition point of the infinite crystal; this maximum increases and sharpens with increasing size of the crystal. Onsager showed that for large n the maximum specific heat is given approximately by

$$C_V/nmk \simeq 0{\cdot}4945 \ln n + 0{\cdot}1879, \qquad (99)$$

and it occurs at a temperature differing by $0(n^{-2} \ln n)$ from T_c for the infinite lattice. The formula extrapolated by Kramers and Wannier (1941) from calculations for finite crystals with $n=1, 2, 3, 4, 5, 6$ is quite close to (99).

(v) *The mean ordered length of a finite crystal.* For an infinite crystal below the Curie temperature there is long-range order, and the majority of spins will point either in direction 1 or in direction 2. However, for a strip of finite width this is no longer the case, and for a long strip equal numbers of spins will point in each direction on the average. We should nevertheless expect them to fall into blocks of opposite order, and the formulae for the boundary tension enable us to estimate the mean length of such an ordered region. The partition function of a boundary of finite width n between regions of opposite order is approximately $\lambda_b{}^n$ and this represents, by Boltzmann's principle, the probability of such a boundary occurring at a given section of the strip at temperature T. Hence the mean length between such boundary occurrences is given from the theory of recurrent events in probability (Feller 1950) by

$$l_0=\lambda_b{}^{-n}=\exp[2n(K-K'^*)]=[\exp(2K)\tanh K']^n. \quad . \quad (100)$$

Clearly when n is large $l_0 \gg n$, and the estimate (100) is then significant.

3.5.2. *The development of Kaufman and Onsager*

In 1949 Bruria Kaufman showed that the algebra required for the determination of the eigenvalues of $\mathbf{V}$ was that of the spin representations of the orthogonal group, the general theory of which had been formulated previously by Brauer and Weyl (1935). The matrix $\mathbf{V}$ is a 2^n-dimensional spin representative of a $2n$-dimensional rotation (i.e. orthogonal matrix), the angles of rotation being complex. The problem is thus reduced to the diagonalization of a $2n$-dimensional orthogonal matrix, and considerations of symmetry resolve this into a product of n plane rotations. The eigenvalues are again found from the solution of n quadratic equations. In addition the matrix of eigenvectors which diagonalizes $\mathbf{V}$ is determined, and this can be used to calculate the degree of order at various distances.

Although the procedure may be standard, it is difficult for anyone without specialized algebraic knowledge to follow. We shall, therefore, again summarize the main conclusions.

(i) *The exact partition function for a torus.* The complete set of eigenvalues has already been given in (95). Hence the exact partition function for an $m\times n$ lattice wrapped on a torus can be written down from (2)

$$Z_{m,n}=\tfrac{1}{2}(2\sinh 2K)^{mn/2}\left\{\prod_{r=1}^{n} 2\cosh(m\gamma_{2r-1}/2)+\prod_{r=1}^{n} 2\sinh(m\gamma_{2r-1}/2)\right.$$
$$\left.+\prod_{r=1}^{n} 2\cosh(m\gamma_{2r}/2)+\prod_{r=1}^{n} 2\sinh(m\gamma_{2r}/2)\right\}. \quad . \quad . \quad . \quad (101)$$

For large n we have seen in § 3.5.1 that $\gamma_{2r+1}\simeq\gamma_{2r}$ $(r\neq 0)$,

$$\gamma_0\simeq\gamma_1 \text{ for } T<T_c, \quad \text{and} \quad \gamma_0\simeq-\gamma_1 \text{ for } T>T_c.$$

Therefore the two products containing $\cosh(m\gamma/2)$ as factors are approximately equal (except for temperatures very near T_c) while the two products with $\sinh(m\gamma/2)$ are approximately equal for $T<T_c$ but cancel out approximately for $T>T_c$. Thus we have

$$\left.\begin{aligned} Z_{m,n} &\simeq (2\sinh 2K)^{mn/2}\prod_{r=1}^{n} 2\cosh(m\gamma_{2r-1}/2) \\ &\quad\times\left[1+\prod_{r=1}^{n}\tanh(m\gamma_{2r-1}/2)\right] \quad (T<T_c), \\ Z_{m,n} &\simeq (2\sinh 2K)^{mn/2}\prod_{r=1}^{n} 2\cosh(m\gamma_{2r-1}/2), \quad (T>T_c). \end{aligned}\right\} \quad . \quad (102)$$

Also for large m, $2\cosh(m\gamma_{2r-1}/2)$, $\exp(m\gamma_{2r-1}/2)$, and the product of the $\tanh(m\gamma_{2r-1}/2)$ is equal to 1 (except in the immediate neighbourhood of T_c). Hence

$$Z_{m,n}\simeq\begin{cases} 2\lambda_{\max}{}^{m}, & T<T_c, \\ \lambda_{\max}{}^{m}, & T>T_c. \end{cases} \quad . \quad . \quad . \quad . \quad . \quad (103)$$

We thus see that the approximation of considering only the largest eigenvalue is a good one as long as m and n are large; the factor 2 arising for $T<T_c$ corresponds to the twofold degeneracy in $\lambda_{\max}$ in the largest eigenvalue approximation.

(ii) *The degree of order.* It was shown in § 3.3.1 that a knowledge of the complete set of eigenvalues and eigenvectors of $\mathbf{V}$ enabled the degree of order to be determined between any two lattice points. This can be conveniently expressed in terms of the matrices $\mathbf{s}_\nu$ defined in (87). Each $\mathbf{s}_\nu$ is a diagonal matrix of order 2^n with $+1$ for all of the 2^{n-1} components in which $\sigma_\nu=1$, and with -1 for all of the components in which $\sigma_\nu=-1$. Thus the trace of $\mathbf{s}_\nu\mathbf{V}^m$ is obtained by multiplying all diagonal components of $\mathbf{V}^m$ with $\sigma_\nu=+1$ by $+1$, and all diagonal components with $\sigma_\nu=-1$ by -1, and therefore

$$\langle\sigma_\nu\rangle=\frac{\mathrm{Trace}\,(\mathbf{s}_\nu\mathbf{V}^m)}{\sum_{i=1}^{2^n}\lambda_i^m}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (104$$

Similarly the correlation between spin ν in layer 1 and spin ρ in layer h is obtained from (23) by summing the product of the $\alpha\beta$ component of $\mathbf{V}^h$ with the $\beta\alpha$ component of $\mathbf{V}^{m-h}$ over all configurations α with a given value of spin ν and β with a given value of spin ρ. It is easy to see that trace $(\mathbf{s}_\nu\mathbf{V}^h\mathbf{s}_\rho\,\mathbf{V}^{m-h})$ gives the factors ± 1 according to the appropriate values of the spins $\sigma_{1\nu}$ and $\sigma_{h\rho}$, and hence that

$$\langle\sigma_{1\nu}\sigma_{h\rho}\rangle=\frac{\mathrm{Trace}\,(\mathbf{s}_\nu\mathbf{V}^h\mathbf{s}_\rho\mathbf{V}^{m-h})}{\sum_{i=1}^{2^n}\lambda_i^m}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (105)$$

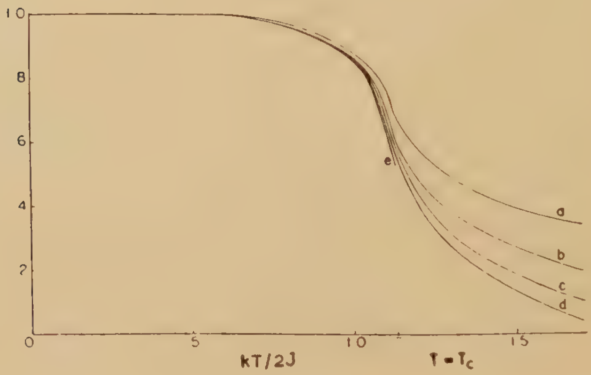
Kaufman and Onsager applied their general theory of the diagonalization of $\mathbf{V}$ to the evaluation of these averages. The details of the algebraic manipulations are quite involved, and the resulting correlations are expressed as determinants of functions which can be reduced to elliptic integrals in the symmetric case $K=K'$. The nearest neighbour correlation

$\langle\sigma_1\sigma_2\rangle$ is equivalent to the energy; and as the distance apart becomes very large the correlation $\langle\sigma_1\sigma_k\rangle$ approaches the long-range order $\mathscr{S}_\infty$, which has been evaluated exactly, and will be discussed shortly. All the intermediate correlations lie between these two bounding curves. Kaufman and Onsager evaluated exactly the correlations $\langle\sigma_1\sigma_2\rangle\langle\sigma_{11}\sigma_{22}\rangle\langle\sigma_1\sigma_3\rangle\langle\sigma_{11}\sigma_{23}\rangle$ and these are shown graphically in fig. 20. At the Curie point it seems that all the correlation functions have a singularity similar to the energy with an infinite slope.

For the correlations $\langle\sigma_1\sigma_k\rangle$ along a given row a general formula can be obtained for all k in the form

$$(-1)^k\langle\sigma_1\sigma_{k+1}\rangle=\cosh^2 K^*\Delta_k+\sinh^2 K^*\Delta_{-k}, \quad . \quad . \quad (106)$$

Fig. 20



Correlations for small distances as functions of temperature. (*a*) $\langle\sigma_1\sigma_2\rangle$, (*b*) $\langle\sigma_{11}\sigma_{22}\rangle$, (*c*) $\langle\sigma_1\sigma_3\rangle$, (*d*) $\langle\sigma_{11}\sigma_{23}\rangle$, (*e*) $\langle\sigma_1\sigma_4\rangle$. All have infinite slope at T_c (after Kaufman and Onsager).

Where Δ_k and Δ_{-k} are Toeplitz determinants of order k whose elements can be reduced to elliptic integrals. At the Curie point the following approximations are reasonable†:

$$\left.\begin{aligned}|\Delta_k|&=\frac{2}{\pi}\prod_{s=1}^{k-1}\frac{\Gamma(s+1)\Gamma(s+1)}{\Gamma(s+\frac{1}{2})\Gamma(s+\frac{3}{2})},\\ |\Delta_{-k}|&=\frac{2}{\pi}\prod_{s=1}^{k-1}\frac{\Gamma(s+1)\Gamma(s+1)}{\Gamma(s+\frac{3}{2})\Gamma(s+\frac{5}{2})}.\end{aligned}\right\} \quad . \quad . \quad . \quad (107)$$

Hence for large k the correlation at the critical point $\simeq A/k^{1/4}$ and tends to zero very slowly as $k\to\infty$.

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†In the paper by Kaufman and Onsager the products are taken to $s=k$ but Dr. M. E. Fisher has pointed out that this is incorrect.

Onsager (private communication) has also derived an expression for the order along a main diagonal for the general anisotropic case which is much simpler than (106). In fact if a_r are defined by

$$\left[\frac{\sinh 2K \sinh 2K' - \exp(i\omega)}{\sinh 2K \sinh 2K' - \exp(-i\omega)}\right] \equiv \sum_{r=-\infty}^{\infty} a_r \exp(ir\omega), \quad . \quad (108)$$

so that the a_r are Fourier coefficients of this function, the order along a main diagonal is given by a single Toeplitz determinant

$$D_k = \begin{vmatrix} a_0 & a_1 & a_2 \cdots\cdot & a_{k-1} \\ a_1 & a_0 & a_1 \cdots\cdot & a_{k-2} \\ a_{-2} & a_{-1} & a_0 \cdots\cdot & a_{k-3} \\ \cdots & \cdots & \cdots & \cdots \\ a_{-(k-1)} & a_{-(k-2)} & \cdots\cdot & a_0 \end{vmatrix}. \quad . \quad . \quad . \quad (109)$$

For this determinant the first equation of (107) is exact so that the correlations at the critical point along a diagonal $\simeq 0{\cdot}645/k^{1/4}$ and the asymptotic form is approached very rapidly.

In the previous section we derived an estimate of the mean range over which order persists above the Curie point in the form $1/[2(K^* - K')]$; this is valid in the direction of interaction J, and the corresponding expression in direction J' is $1/[2(K^* - K')]$. In intermediate directions of angle ϕ Onsager in his first paper conjectured the implicit formula,

$$\cosh 2K \cosh 2K' - \sinh 2K \cosh(\beta \sin\phi) - \sinh 2K' \cosh(\beta\cos\phi) = 0, \quad . \quad . \quad . \quad (110)$$

for the mean range $1/\beta$ of the order. This would imply that, with $K = K'$, for temperatures near the critical point the order spreads out isotropically, whereas for high temperatures it spreads out along the links of the lattice (fig. 21). The exact computations available so far confirm this general behaviour. Knowledge of the mean range of order as a function of temperature provides information on the temperature variation of the correlation functions, and this has been used by Fisher (1959 b) to derive an expression for the high temperature susceptibility near the Curie point.

(iii) *The long-range order.* There are two independent approaches to the question of long-range order. The first considers the limit of the correlation function $\langle\sigma_1\sigma_k\rangle$ defined above as $k \to \infty$. The second evaluates the spontaneous magnetization by a small perturbation of the no-field solution for $T < T_c$; the spontaneous magnetization is equal to the long-range parameter R (defined in § 3.3) as will be shown in § 3.6.4.

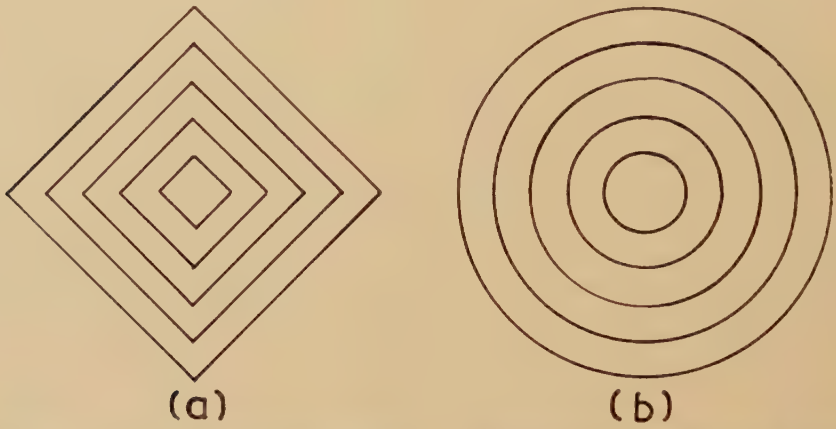
The exact formula for the long-range order was first given by Onsager (Florence Conference on Statistical Mechanics 1949) although he provided no details of his calculation. The result can be derived from (109) or corresponding determinants obtained by Potts and Ward (see § 3.5.3) using the theory of Toeplitz forms†. The only published derivation (using the perturbation method) is due to Yang (1952) (see also Chang 1952).

The result can be put in the remarkably simple form (Potts 1952):

$$\left.\begin{aligned} R^8 &= 1-\sinh^2 2K'^*/\sinh^2 2K \\ &= 1-16z^2z'^2/(1-z^2)^2(1-z'^2)^2 \end{aligned}\right\} \operatorname*{Lt}_{k\to\infty} \langle\sigma_1\sigma_k\rangle = R^2. \qquad (111)$$

R differs only slightly from unity except in the immediate neighbourhood of the Curie point; for the symmetric lattice its value near the Curie point is $\simeq 1{\cdot}22241(1-T/T_c)^{1/8}$. The spontaneous magnetization is represented graphically in fig. 32.

Fig. 21


(a) (b)

Anisotropy in the propagation of order. At high temperatures order spreads out along the links of the lattice with little correlation and the contours of constant order are as shown in (*a*). Near the Curie point the correlation becomes very marked, and the contours are circles, as in (*b*).

3.5.3. *The combinatorial method of Kac and Ward*

The method of Kac and Ward is elementary in the sense that no detailed algebraic knowledge is required other than properties of determinants. It undoubtedly provides the simplest derivation of the partition function and other properties of two-dimensional Ising models, and has been able to reproduce all results obtained by other means. The method also sheds considerable light on the topological conditions which give rise to an exact solution in two dimensions and shows that they are absent in three dimensions. However, it is also fair to state that only the knowledge of the existence and form of Onsager's solution enabled Kac and Ward to drive their ideas to a satisfactory conclusion.

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†For further information on this subject see Polya and Szegö (1925), Kac *et al.* (1953), Grenander and Szegö (1958). I am indebted to Professor E. W. Montroll for these references.

(i) *Partition function for a large net.* Kac and Ward start from the formula (35) giving the partition function for the Ising model in terms of closed polygons on the lattice. For a lattice of n horizontal and m vertical links connected together on a torus this formula is

$$Z_{mn}{}^{I}=2^{mn}(\cosh K\cosh K')^{mn}\left[1+\sum_{r=1}^{n}\sum_{s=1}^{m}p(r,s)v'^{r}v^{s}\right],$$

$$(v=\tanh K,\quad v'=\tanh K')\qquad .\ .\ .\ .\ .\ \quad (112)$$

where $p(r,s)$ is the number of closed polygons with even vertices which can be constructed on the lattice from r horizontal and s vertical links (fig. 7). Following Kac and Ward we shall endeavour to construct a determinant each term of whose expansion corresponds uniquely to one of the configurations in the sum (112).

Denote the elements of the determinant by A_{PQ}. Then any term in $\det \mathbf{A}(\equiv\Delta)$ is of the form

$$\pm(A_{1P_1}A_{2P_2}\cdots A_{NP_N})$$

and can be broken up into cycles

$$\pm(A_{P_1P_2}\cdots A_{P_aP_1})(A_{Q_1Q_2}\cdots A_{Q_bQ_1})\cdots(A_{R_1R_2}\cdots A_{R_cR_1}).\qquad .\quad (113)$$

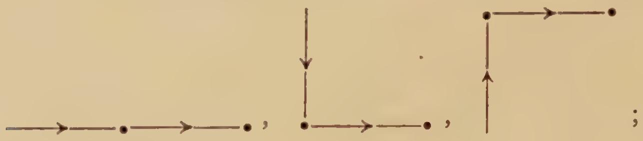
We would like each cycle to represent one closed polygon, and we must choose the elements A_{PQ} so that only polygons represented in (112) enter in the expansion of Δ. Let us take for the suffixes P, Q the links in the lattice, but directions must also be specified if we are to trace out polygons; there are four links directed towards each point $(i,\ j)$ of the lattice the directions being right $R(\rightarrow)$, left $L(\leftarrow)$, up $U(\uparrow)$, or down $D(\downarrow)$. Thus each suffix P corresponds to a directed bond in the lattice $(i,\ j,\ \Gamma)$ where Γ has four possible values R, L, U, D; Δ is then of order $4mn$. We take $A_{PP'}$ to be zero unless P, P' correspond to nearest neighbour lattice points, i.e. unless

$$i=i'\pm1,\quad j=j'\quad \text{or}\quad i=i',\quad j=j'\pm1.$$

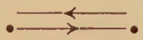
We now notice that the determinant counts oriented polygons, both clockwise and anticlockwise orientations being possible, and being counted separately. Kac and Ward were impressed by the fact that in the formula (101) of Kaufman for the p.f. (partition function) of a net wrapped on a torus m and n do not enter symmetrically and $m/2$ enters naturally rather than m; thus the square of the p.f. might prove considerably simpler than the p.f. itself. If we now square Z_{mn} in (112) we can represent this as a superposition of two independent sets of polygons on one another, and we can take one set to be oriented clockwise and the other anticlockwise (fig. 22).

Now in Δ every directed link occurs exactly once in each term, whereas in the polygon expansion only links forming parts of polygons occur. This difficulty is readily surmounted by taking $A_{PP}=1$, and hence making all the unused bonds in the polygon expansion correspond to single cycles in Δ.

We specified above that $A_{PP'}$ is only non zero when P and P' correspond to nearest neighbour lattice points. But we can be more particular now in regard to the possible direction Γ' of P'. Thus if $i'=i+1, j'=j$ then Γ' must be R $(\longrightarrow)$; the only non-zero values can be represented graphically as

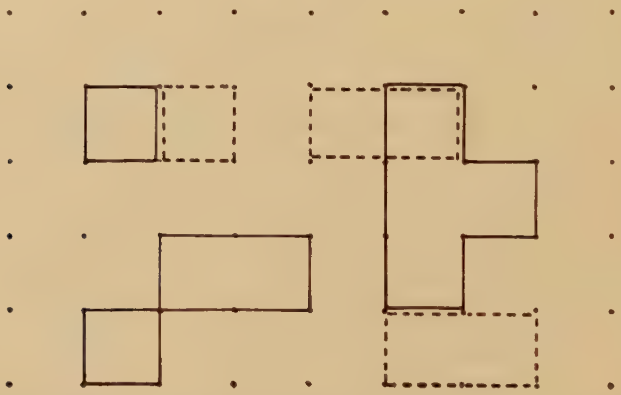


immediate reversals



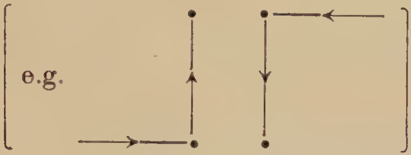
must be excluded and the corresponding elements are zero. Hence of the 16 terms in the 4×4 section corresponding to (i,j) and $(i+1,j)$ only three terms are non-zero, $A(i,j,R;\ i+1,j,R)$, $A(i,j,D;\ i+1,j,R)$, and $A(i,j,U;\ i+1,j,R)$. Analogous results can be derived for the other nearest neighbours of P.

Fig. 22

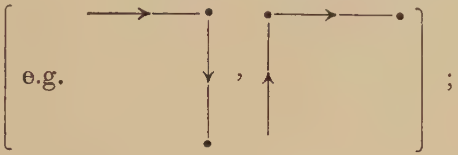


Z_{mn}^2 is represented by a superposition of two sets of polygons the first oriented clockwise (full lines) and the second anticlockwise (broken lines).

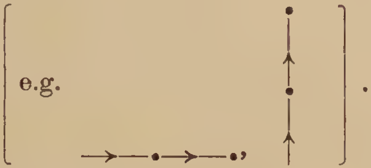
The actual values of the elements of A must now be chosen so as to give the correct factor $v'^r v^s$ to the term in Δ corresponding to $p(r,s)$. Clearly any term corresponding to a given link must have the appropriate v or v' (e.g. in the above example all the terms will contain the factor v'). But the terms in Δ are counted with $\pm$ sign according as the corresponding permutation is odd or even, and we may therefore have to insert an additional factor to ensure that terms corresponding to closed polygons are always counted as positive. Now it is well known that a cycle with an even number of terms corresponds to an odd permutation and hence to a minus sign in Δ; thus the factor must be chosen so that an additional factor -1 accompanies every even closed cycle. It will easily be verified that this can be achieved by taking a factor $\exp(\pi i/4)$ for elements involving an anti-clockwise turn of $\pi/4$



and $\exp(-\pi i/4)$ for those involving a clockwise turn of $\pi/4$



other elements remain unchanged



For example the portion of Δ corresponding to (i,j) and $(i+1,j)$ is

$$\mathbf{\Theta}(1,0)=\begin{array}{c|cccc|} & R & L & U & D \\ R & v' & 0 & 0 & 0 \\ L & 0 & 0 & 0 & 0 \\ U & v'\alpha^{-1} & 0 & 0 & 0 \\ D & v'\alpha & 0 & 0 & 0 \end{array} \qquad [\alpha=\exp(\pi i/4)].$$

Similarly the three portions corresponding to (i,j) and $(i-1,j)$, $(i,j+1)$, $(i,j-1)$ are respectively

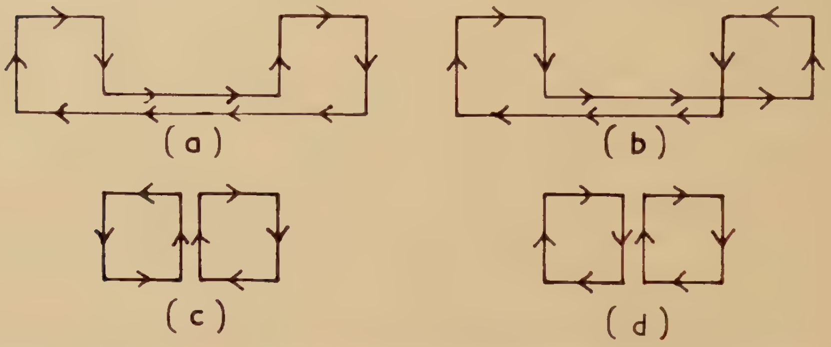
$$\mathbf{\Theta}(0,1)=\begin{vmatrix} 0 & 0 & v\alpha & 0 \\ 0 & 0 & v\alpha^{-1} & 0 \\ 0 & 0 & v & 0 \\ 0 & 0 & 0 & 0 \end{vmatrix} \quad \mathbf{\Theta}(-1,0)=\begin{vmatrix} 0 & 0 & 0 & 0 \\ 0 & v' & 0 & 0 \\ 0 & v'\alpha & 0 & 0 \\ 0 & v'\alpha^{-1} & 0 & 0 \end{vmatrix}$$

$$\mathbf{\Theta}(0,-1)=\begin{vmatrix} 0 & 0 & 0 & v\alpha^{-1} \\ 0 & 0 & 0 & v\alpha \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & v \end{vmatrix} \qquad \ldots \quad (114)$$

The construction of the appropriate determinant is now complete. For graphs consisting of simple closed polygons with no point or side in common it is clear that the counting performed by the determinant is correct. But when we begin to consider graphs containing polygons with points and sides in common, substantial difficulties remain in establishing that the counting is always correct. In fact the terms in the expansion of the determinant do not correspond identically with those of the oriented graphs, but in all cases which have been investigated in detail the results are equivalent. Sometimes the determinant counts additional terms which cancel out in pairs (fig. 23 *a*, *b*); and sometimes it does not count the correct polygons but other configurations which are equivalent (fig. 23 *c*, *d*). (Several additional examples are given in Newell and Montroll 1953). But we shall now show that the partition function obtained from Δ is identical with that derived by Onsager, so it seems clear that such cancellations and rearrangements always occur exactly†.

The matrix $\mathbf{A}$ is clearly cyclic in both dimensions all lattice points being equivalent. Let us denote any eigenvector of $\mathbf{A}$ by $\mathbf{X}$; this can be divided into mn sections $\mathbf{X}_{i,j}$ each of length 4 units corresponding to the lattice point (i, j). The eigenvectors of $\mathbf{A}$ are then given by $\mathbf{X}_{i,j}=\mathbf{a}\epsilon^{i}\eta^{j}$ where ϵ is an nth root, and η an mth root of unity, and $\mathbf{a}$ is a 4×1 vector.

Fig. 23



There is not always an exact correspondence between terms of Δ and $Z_{mn}{}^2$ but a correspondence of final results. (*a*), (*b*) represent curves absent in $Z_{mn}{}^2$ which cancel in pairs in Δ. Only (*c*) are present in $Z_{mn}{}^2$ whereas Δ counts only (*d*).

The matrix $\mathbf{A}$ thus reduces to the 4×4 matrix

$$I_4+\epsilon\boldsymbol{\Theta}(1,0)+\epsilon^{-1}\boldsymbol{\Theta}(-1,0)+\eta\boldsymbol{\Theta}(0,1)+\eta^{-1}\boldsymbol{\Theta}(0,-1), \quad . \quad (115)$$

and its determinant is found by multiplying the mn 4×4 determinants of (115) for n possible values of ϵ and m of η. We find that

$$\Delta=\prod_{r=1}^{n}\prod_{s=1}^{m}\{(1+v^2)(1+v'^2)+2v'(1-v^2)\cos(2r\pi/n) + 2v(1-v'^2)\cos 2s\pi/m)\}, \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (116)$$

and hence for large m, n

$$Z_{mn}{}^2\simeq 2^{2mn}\prod_{r=1}^{n}\prod_{s=1}^{m}\{\cosh 2K\cosh 2K'+\sinh 2K'\cos(2r\pi/n) + \sinh 2K\cos(2s\pi/m)\}. \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (117)$$

---

†This has been established rigorously recently by S. Sherman following some ideas initially put forward by R. P. Feynman. See "Combinatorial Aspects of the Ising Model for Ferromagnetism" to appear in *J. math. Phys.*

Taking logarithms and proceeding to the limit as $m,\ n \to \infty$ we re-derive for the partition function per spin the Onsager formula

$$\ln(\lambda/2) = \tfrac{1}{2}\pi^{-2}\int_0^\pi\int_0^\pi \ln(\cosh 2K \cosh 2K' - \sinh 2K \cos\omega - \sinh 2K' \cos\omega')\, d\omega\, d\omega'. \quad . \quad . \quad . \quad . \quad . \quad . \quad (118)$$

(ii) *End effects.* We have assumed throughout our work that end effects can be ignored, i.e. that changes in the partition function arising from finite boundaries become negligible for large m and n. Temperley (1957) has shown that this can be established rigorously. The counting determinant for a finite lattice is only different from Δ in lattice points corresponding to the boundary, but its cyclic character is destroyed. Temperley shows how to combine cyclic solutions so as to satisfy the boundary conditions, and concludes that even at the critical point the changes in Z_{mn} are only or order m or n.

(iii) *Exact partition function for a torus.* The exact partition function for a finite torus can also be established by the combinatorial method, as was shown by Potts and Ward (1955). The error introduced in the counting determinant above for a finite net arises from graphs which loop the torus, and which may be counted with the wrong sign. The wrongly counted graphs always include one or more of three simple loops

(*a*) a horizontal loop with n bonds counted with sign $(-1)^{n-1}$,

(*b*) a vertical loop with m bonds counted with sign $(-1)^{m-1}$,

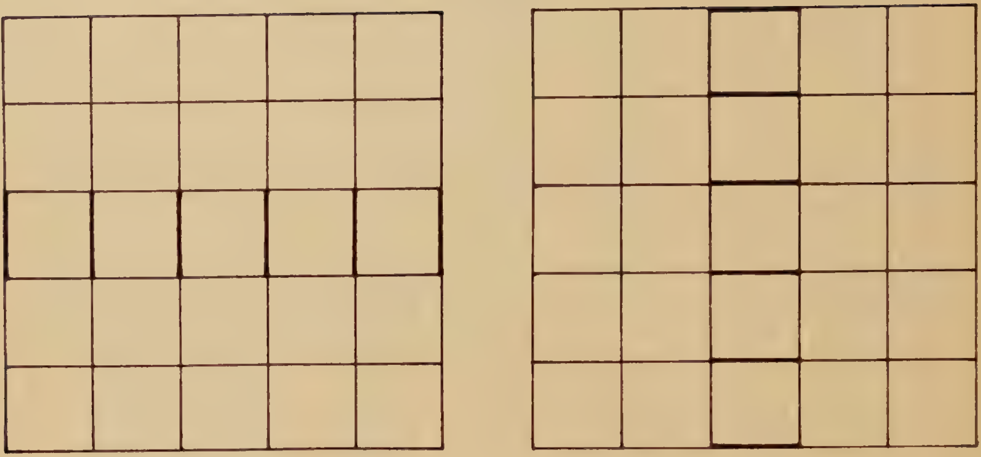
(*c*) a combination of these two with $(m+n)$ bonds counted with sign $(-1)^{n+m-1}$.

It is evident that a restriction to even or odd $n,\ m$ is not sufficient to correct these signs. However, by replacing K and K' by $-K,\ -K'$ the horizontal loops will now be counted with sign $(=1)^{n-1}\ (-1)^n = -1$; similarly all the other loops will be counted with sign -1. Our purpose must now be to correct the negative sign for all such loops.

Potts and Ward made use of the following device. Let us denote Δ by $P_1(K,\ K')$. Consider the counting determinant which changes the sign of all interactions in the lattice except one row of vertical interactions (fig. 24*a*); let us denote this by $P_2(-K,\ -K')$. Then this counts correctly all graphs without loops, vertical loops are counted with a positive sign, horizontal with a negative sign, and vertical and horizontal loops with a positive sign. Define similarly $P_3(-K,-K')$ for the counting determinant which changes the sign of all interactions in the lattice except one column of horizontal interactions (fig. 24*b*); and $P_4(-K,\ -K')$ for the corresponding determinant leaving both a row and a column unchanged. Then the counting of loops is summarized in table 1.

At high temperatures we must count all loops with a positive sign. But at low temperatures we use the duality transformation (§ 3.4.2); from eqn. (38) we notice that a factor 2 enters, because of the degeneracy of the lowest energy state, but configurations which loop the torus singly do not give rise to a low temperature configuration and must not be

Fig. 24



(a) (b)

(*a*) $P_2(-K, -K')$ corresponds to a change in sign of all vertical interactions except those heavily lined ; (*b*) $P_3(-K, -K')$ corresponds to a change in sign of all horizontal interactions except those heavily lined.

Table 1. Counting of Loops on a Finite Rectangular Lattice Wrapped on a Torus

Type of graph	Counting determinant				Z_{mn}	
	P_1	P_2	P_3	P_4	$T<T_c$	$T>T_c$
Vertical loop	$-$	$+$	$-$	$+$	0	1
Horizontal loop	$-$	$-$	$+$	$+$	0	1
Vertical and horizontal loop	$-$	$+$	$+$	$-$	0	1
Other graphs	$+$	$+$	$+$	$+$	2	1

counted. It will be seen from table 1 that all the counting will be correct for the expression.

$$Z=\tfrac{1}{2}\{\pm\sqrt{P_1(-K,-K')}+\sqrt{P_2(-K,-K')}+\sqrt{P_3(-K,-K')}+\sqrt{P_4(-K,-K')}\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (119)$$

where the $+$ sign is taken at low temperatures and the $-$ sign at high temperatures†.

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†In fact for a finite torus the p.f. is continuous and is adequately specified by the high temperature expansion. However, it is a useful check to verify the formula directly from the low temperature expansion and the duality transformation.

We must now consider the evaluation of the $P_j(-K, -K')$. We noticed that $P_1(-K, -K')$ was cyclic and could be reduced by taking

$$\mathbf{X}_{i+1,j} = \epsilon \mathbf{X}_{i,j}, \quad \mathbf{X}_{i,j+1} = \eta \mathbf{X}_{i,j} \quad (\epsilon^n = \eta^m = 1). \qquad (120)$$

Although $P_2(-K, -K')$ is not cyclic it can be reduced in an analogous fashion. We write

$$\left.\begin{aligned} \mathbf{X}_{i,j+1} &= \delta \mathbf{X}_{i,j}, & j &\neq m, \\ \mathbf{X}_{i,1} &= -\delta \mathbf{X}_{i,m}, & \delta^m &= -1, \\ \mathbf{X}_{i+1,j} &= \eta \mathbf{X}_{i,j}, & & \end{aligned}\right\} \qquad (121)$$

and it will be found that the matrix **A** again reduces to a 4×4 matrix with δ replacing ϵ. The basis of the method will become clear from a study of the eigenvectors of the matrix

$$\mathbf{T}_n = \begin{Bmatrix} 0 & 1 & 0 & \ldots\ldots & 0 & 0 \\ 0 & 0 & 1 & \ldots\ldots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots\cdots & \cdots & \cdots \\ 0 & 0 & 0 & \ldots\ldots & 0 & 1 \\ -1 & 0 & 0 & \ldots\ldots & 0 & 0 \end{Bmatrix}$$

Hence we can write

$$P_2(-K, -K') = \prod_{r=1}^{n} \prod_{s=1}^{m} \{\cosh 2K \cosh 2K' - \sinh 2K' \cos(2r\pi/n) - \sinh 2K \cos[(2s-1)\pi/n]\}. \qquad (122)$$

Similarly $P_3(-K, -K')$ retains ϵ and replaces η by κ where $\kappa^m = -1$; and $P_4(-K, -K')$ replaces ϵ by δ and η by κ.

We can write $P_1(-K, -K')$ in the form

$$P_1(-K, -K') = 2^{2mn} \prod_{r=1}^{n} \prod_{s=1}^{m} \{\cosh 2K \cosh 2K' - \sinh 2K' \cos(2r\pi/n) - \sinh 2K \cos(2s\pi/m)\}$$

$$= (2 \sinh 2K)^{mn} \prod_{s=1}^{n} 4 \sinh^2(m\gamma_{2s}/2) \qquad (123)$$

where the γ_r are as defined in (92), i.e.

$$\cosh \gamma_r = \coth 2K \cosh 2K' - \operatorname{cosech} 2K \sinh 2K' \cos(r\pi/n).$$

Here we have made use of the identity

$$2^m \prod_{r=1}^{m} (\cosh \gamma - \cos 2r\pi/m) = 4 \sinh^2(m\gamma/2). \qquad (124)$$

Proceeding similarly with P_2, P_3, P_4 and defining γ_{2n} appropriately it can be shown that Z_{mn} as given by (119) reduces to (101) as given by Kaufman.

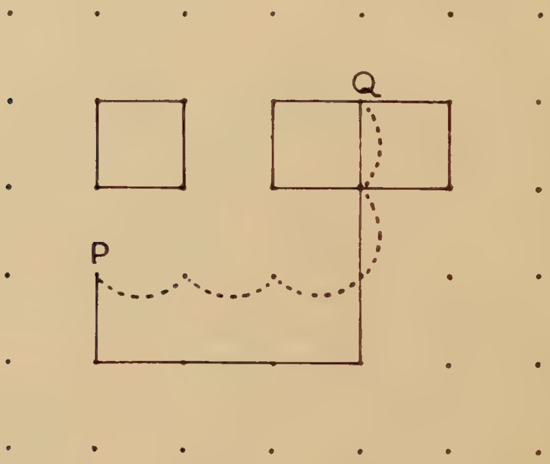
(iv) *The degree of order*. Potts and Ward (1955) also showed that the correlations between spins on different sites, and hence the corresponding degree of order could also be derived readily by the combinatorial method.

If $\mathscr{H}$ is the Hamiltonian for the system then the correlation between spins on sites (2,2) and $(a+2, b+2)$† is given by

$$Z_{mn}\langle\sigma_{2,2}\sigma_{a+2,b+2}\rangle = \sum_{\substack{\text{lattice}\\ \text{sites}}} \sigma_{2,2}\sigma_{a+2,b+2}\exp(-\mathscr{H}/kT). \quad . \quad (125)$$

The exponential in (125) can be expanded as in (33) and the terms represented graphically as in fig. 6. In the absence of a magnetic field the only graphs giving non-zero contributions will be closed polygons with even vertices as before, except that at the points (2, 2) and $(a+2,\ b+2)$ there must be free ends with an odd number of vertices (fig. 25). Potts and Ward converted this into a closed polygon problem of the type considered previously by introducing extra bonds, so as to close the free-ended graph.

Fig. 25



The only graphs to be considered for the correlation between P and Q are those with an odd number of vertices at P, Q and an even number elsewhere. These are converted into closed polygons by the introduction of 'extra' bonds (broken lines).

The extra bonds (shown dotted in fig. 25) consist of a horizontal bonds from $(2, 2)$ to $(a+2, 2)$ and b vertical bonds from $(a+2, 2)$ to $(a+2, b+2)$. We may now write

$$Z_{mn}\langle\sigma_{2,2}\sigma_{a+2,b+2}\rangle = (2\cosh K'\cosh K)^{nm}\coth^a K'\coth^b K\sum\pi(r,s)v'^r v^s, \quad (126)$$

where $\pi(r, s)$ is the number of closed graphs as before, but counting only graphs which include the extra bonds.

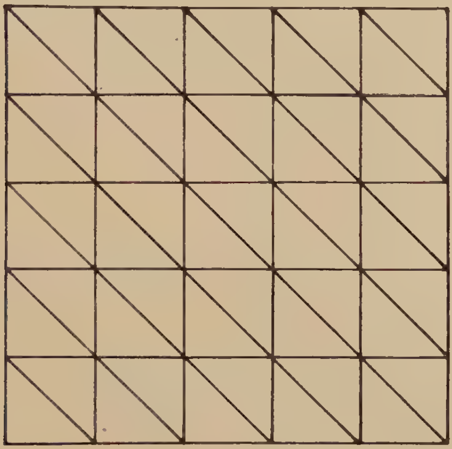
The counting is achieved as before by superimposing the lattice on itself, and taking one set of polygons as oriented clockwise and the other as oriented anticlockwise. This means that the extra bonds must be taken in both directions. The extra bonds are taken into account by bordering Δ with $2(a+b)$ rows and columns corresponding to the two possible directions for each extra bond. The elements are chosen very much as before, but the diagonal elements of the bordering section are taken to be zero, so that these extra bonds must be included in any non-zero term.

---

†This choice is for convenience to avoid boundary effects in the diagrams.

The details of the construction and reduction of the determinant are given by Potts and Ward. The complete identification of their results with those of Kaufman and Onsager, appears to be somewhat involved, but calculation in particular cases showed agreement. The method certainly provides the simplest practical approach to the evaluation of correlations.

Fig. 26



The triangular lattice is topologically equivalent to a rectangular lattice with one second neighbour interaction.

3.5.4. *Exact solutions for other two-dimensional lattices*

(i) *The triangular lattice.* We have seen in § 3.4.3 how the duality and star-triangle transformations enable the Curie point of the triangular lattice to be located. Shortly after the publication of the work of Onsager and Kaufman, several papers appeared independently giving the exact solution for this lattice (Houtappel 1950, Husimi and Syozi 1950, Newell 1950, Temperley 1950, Wannier 1950). Potts (1955) applied the combinatorial method to the triangular lattice, and this leads most directly to the solution. From this point of view the triangular lattice is best considered as a rectangular lattice with a single second neighbour interaction (fig. 26); the lattice can be wrapped on a torus and the procedure is then closely analogous to that of § 3.5.3. The resulting partition function per spin is given (for general interactions K, K', K'') by

$$\left.\begin{aligned} \ln(\lambda/2) = (8\pi^2)^{-1}\int_0^{2\pi}\int_0^{2\pi} \ln\Big\{&CC'C''+SS'S''-S\cos\omega_1\\ &-S'\cos\omega_2-S''\cos(\omega_1+\omega_2)\Big\}\,d\omega_1\,d\omega_2\\ C, C', C'' = \cosh 2K,\quad &\cosh 2K',\quad \cosh 2K''.\\ S, S', S'' = \sinh 2K,\quad &\sinh 2K',\quad \sinh 2K''. \end{aligned}\right\} \quad . \quad (127)$$

It is clear that as $K''\to 0$ we regain the formula (94) for the rectangular lattice.

The physical properties of the ferromagnetic triangular lattice are very similar to those of the quadratic lattice. The singularities in the thermodynamic functions are of the same type, and when $K=K'=K''$ these functions differ only slightly from one another in relative value. As an example of the order of magnitude of this variation the approximate formulae for the specific heats in the neighbourhood of the Curie point for the two lattices are as follows:

$$C_{\text{v}}/Nk \begin{aligned} &\simeq -0{\cdot}4991\ln|T-T_{\text{c}}| \quad \text{(triangular)},\\ &\simeq -0{\cdot}4945\ln|T-T_{\text{c}}| \quad \text{(quadratic)}. \end{aligned} \Bigg\} \quad . \quad . \quad (128)$$

(Houtappel 1950).

An interesting and novel feature of the triangular lattice is the antiferromagnetic solution, and this aspect is discussed in detail by Wannier (1950). Antiferromagnetism does not fit into a triangular lattice and we can readily show that the energy of the lowest state is only one-third of the corresponding ferromagnetic value. First we note that the energy cannot be lower than this value; the net can be completely decomposed into triangles each of which contains three interactions. The best we can achieve within each triangle is to have two spins of one kind and one of another; hence the minimum possible energy is $NJ(J<0)$.

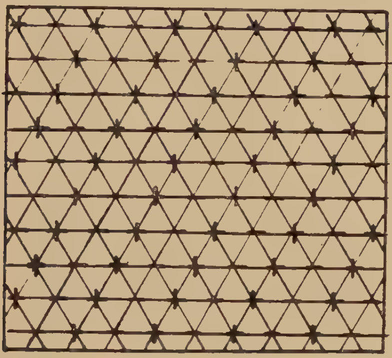
We now construct states with exactly this minimum energy. Figure 27 which consists of alternating rows of positive and negative spins is an example of such a state. Figure 28 shows another arrangement in which the rows can be fitted together at random without changing the energy; the weight of states of this kind is of order $N^{1/2}$, and they do not, therefore, give rise to any entropy. In fig. 29 we have an arrangement with a finite entropy. In this arrangement the correct energy is obtained by an unbalance; each + spin is surrounded by 6 − spins, but each − spin contains 3 + spins and 3 − spins among its neighbours. From this it follows that each of the encircled negative spins can be overturned independently without changing the energy; there are thus at least $2^{N/3}$ independent states.

But this does not exhaust all possible states. It may happen that a trio of neighbouring encircled spins have the same sign (in fact each possible configuration of these spins will occur on the average on one-eighth of the occasions) and that the spin at the centre of the tripod then has equal numbers of + and − spins as its neighbours, and can be reversed without changing the energy.

The number of states is hence increased by a factor $2^{N/12}$. Thus the entropy at absolute zero is greater than

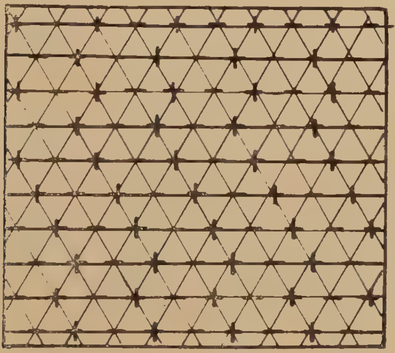
$$\tfrac{5}{12}Nk\ln 2 = 0{\cdot}288811Nk. \quad . \quad . \quad . \quad . \quad . \quad . \quad (129)$$

Fig. 27



A minimum energy anti-ferromagnetic state for the triangular lattice. Rows of positive spins alternate with rows of negative spins.

Fig. 28



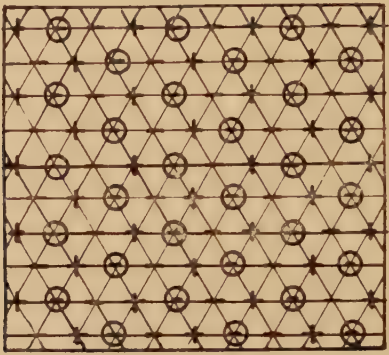
An arrangement of minimum energy in which rows can be stacked at random.

Wannier derived an exact expression for this entropy in the form

$$S(0)/Nk = \frac{3}{\pi}\int_0^{\pi/6} \ln(2\cos\omega)\,d\omega = 0{\cdot}32306. \quad . \quad . \quad . \quad (130)$$

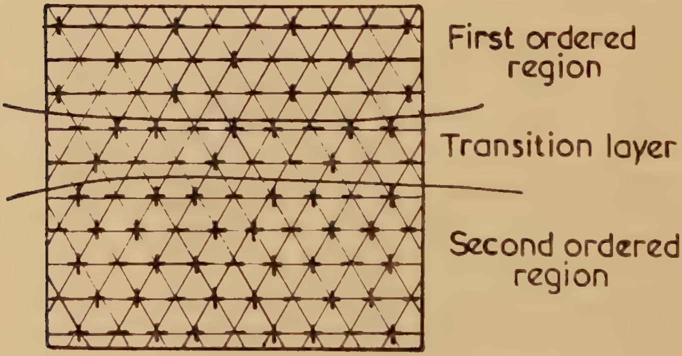
He also pointed out that long-range order was incompatible with a degenerate lowest energy state of the kind described. As seen in fig. 30 it is possible for two states with different order to adjoin being connected by a transition region with the same energy as the ordered regions. It is not surprising therefore that the partition function for an antiferromagnetic triangular lattice (in the absence of a magnetic field) has no singularity, and the specific heat curve is smooth and continuous with no infinity.

Fig. 29



An arrangement of minimum energy having finite entropy. The encircled spins can point in either direction.

Fig. 30



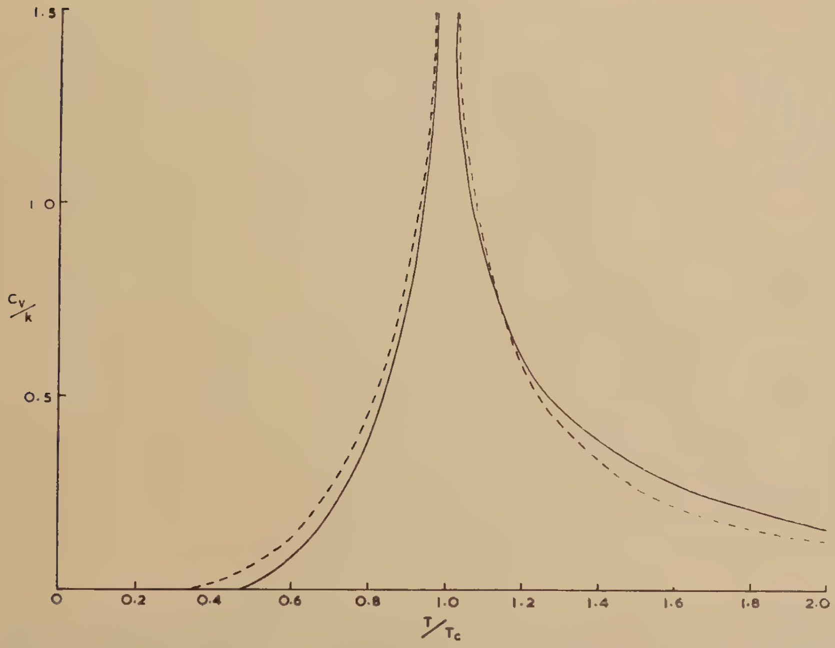
Two adjoining regions having different types of long range order. The energy of the transition layer may be made just as low as that of the ordered regions.

Since the presence of a small magnetic field at $T=0$ would cause a large change in the number of spins pointing in the direction of the field, we should expect the susceptibility of the triangular lattice to be infinite at $T=0$. In some respects, therefore, the behaviour of the antiferromagnetic triangular lattice in zero field is analogous to the behaviour of an antiferromagnetic linear chain in a critical field (§ 3.2.1).

(ii) *The honeycomb lattice.* The solution for the honeycomb lattice can be obtained by applying the star-triangle transformation to the solution for the triangular lattice. The partition function is given by

$$\ln(\lambda/2) = (16\pi^2)^{-1}\int_0^{2\pi}\int_0^{2\pi} \ln \tfrac{1}{2}\{CC'C''+1-S'S''\cos\omega_1 - S''S\cos\omega_2 - SS'\cos(\omega_1-\omega_2)\}\,d\omega_1\,d\omega_2. \quad . \quad . \quad (131)$$

Fig. 31



A comparison of the specific heats of the honeycomb and quadratic lattices.
——————— honeycomb ; – – – – – – – – quadratic.

The physical properties of the honeycomb lattice are again closely similar to those of the quadratic lattice. The specific heat approximation near the Curie point is (Houtappe 1950).

$$C_V/Nk \simeq -0{\cdot}4781 \ln|T-T_c|. \quad . \quad . \quad . \quad . \quad . \quad . \quad (132)$$

The specific heats of the honeycomb and quadratic lattices are compared in fig. 31.

Several properties of the quadratic, triangular and honeycomb lattices can be combined into one general formula. Thus Onsager noted (Wannier 1945) that the Curie points of all three lattices are given by

$$\mathrm{gd}\, 2K = \pi/q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (133)$$

where gd denotes the gudermanian, $[\mathrm{gd}\, x = \sec^{-1}(\cosh x) = \tan^{-1}(\sinh x)]$ and q is the coordination number of the lattice. Similarly we have seen that the inversion transformation can be put in the form (59) which applies to all three lattices. Finally Potts (1952) showed that the spontaneous magnetization of the triangular lattice could be put in the form (111), the appropriate transformation variables being given by the inversion transformation (58) of § 3.4.3 ($K \to K^*$). We may thus write for both quadratic and triangular lattices

$$(I/m)^8 = 1 - (v^{-1} - v)^2/(z^{-1} - z)^2, \quad . \quad . \quad . \quad . \quad (134)$$

using the v variables of § 3.4.2, § 3.4.3; from (60) the spontaneous magnetization of the triangular lattice is given by

$$(I/m)^8 = 1 - \frac{16z^6}{(1+3z^2)(1-z^2)^3}. \quad . \quad . \quad . \quad . \quad (135)$$

In order to derive the spontaneous magnetization of the honeycomb lattice Naya (1954) introduced the idea of a 'semi-ferromagnetic' honeycomb lattice in which one of the two triangular sub-lattices into which the honeycomb lattice can be divided (fig. 11) consists of spins with normal magnetic moment m, and the other consists of spins with zero magnetic moment. Naya showed that the spontaneous magnetization of the semi-ferromagnetic honeycomb lattice was exactly half that of the normal ferromagnetic honeycomb lattice. Now the non-magnetic spins could be removed by the star-triangle transformation (§ 3.4.3) in the presence of a magnetic field (§3.4.5), and a relation could thus be derived between the spontaneous magnetization of the triangular lattice and the semi-ferromagnetic honeycomb lattice (see also Fisher 1959 a). It was found that the spontaneous magnetization of the honeycomb lattice could also be put into the form (134), the appropriate transformation variable being given by (62). Hence for this lattice

$$(I/m)^8 = 1 - \frac{16z^3(1+z^3)}{(1-z)^3(1-z^2)^3}. \quad . \quad . \quad . \quad . \quad . \quad (136)$$

The spontaneous magnetization varies only slightly from one lattice to another among the three lattices considered so far, as will be seen from fig. 32.

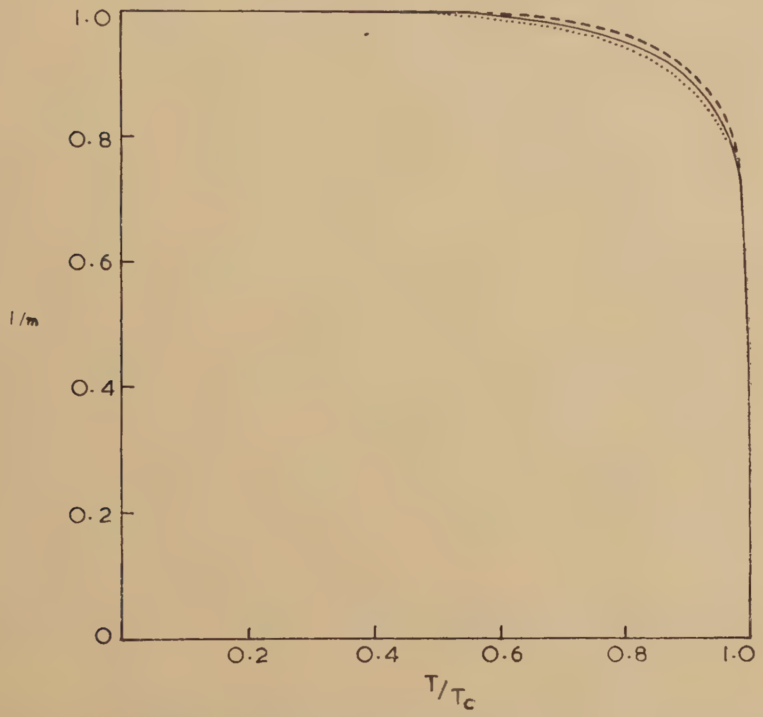
The honeycomb lattice has a Curie point for all values and signs of the interaction parameters.

(iii) *The kagomé lattice.* In § 3.4.4 we showed how the decoration transformation could be used to derive a relation between the honeycomb and kagomé lattices in the presence of a magnetic field. Hence the thermodynamic properties of the kagomé lattice can be derived from those of the honeycomb lattice (Syozi 1951, Naya 1954). The kagomé lattice does not satisfy the relations (59), (133), (134) derived for the other two-dimensional lattices. Its antiferromagnetic properties are similar to those of the triangular lattice (Kano and Naya 1953), and it possesses a finite entropy, $0{\cdot}50183Nk$ at the absolute zero.

(iv) *General treatment of two-dimensional lattices.* A general approach to a large variety of two-dimensional lattices, which includes all the lattices discussed so far, and can be applied to many others, was put forward by Utiyama in 1951 (see also Syozi 1955 a). The methods of Kaufman and

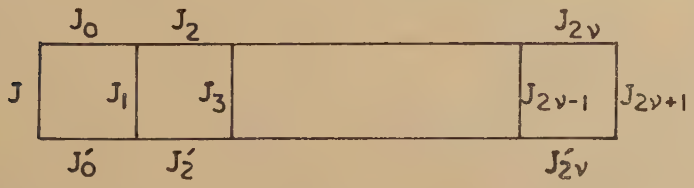
Onsager can equally well be used for a chequer lattice formed by replacing all the black squares of the chessboard by one and the same elementary figure. The elementary figure consists of a rectangle with ν vertical crosspieces (fig. 33). By varying the interaction parameters, and taking

Fig. 32



The spontaneous magnetizations of different lattices. - - - - - - - honeycomb; ———— quadratic ; · · · · · · · · triangular.

Fig. 33



Elementary figure suggested by Utiyama to be placed on all black squares of the chessboard.

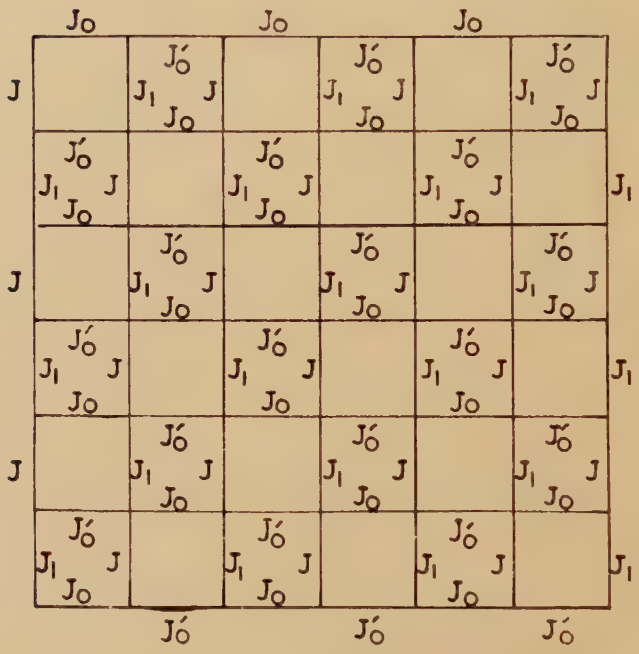
some as 0 or ∞, we can generate different lattices. For example with $\nu=0$, $J=\infty$, $J_1=0$, or $J=J_1$, $J_0=J_0'$ gives the quadratic lattice; $J=0$ gives the honeycomb lattice; $J=\infty$ gives the triangular lattice (fig. 34). With $\nu=1$ $J=\infty$ corresponds to the kagomé lattice (fig. 35); and $J_3=0$

gives the 4–8 lattice (fig. 36) which is of interest since, although all points are equivalent, all bonds are not equivalent; in this respect the 4–8 lattice resembles the three-dimensional close-packed hexagonal lattice.

The partition function per spin can be written down quite generally in terms of the interaction parameters. Thus for $\nu=0$ we can write, using a notation analogous to (127),

$$\ln(\lambda/\sqrt{2})=\frac{1}{2(2-n_\infty)}\frac{1}{(2\pi)^2}\int_0^{2\pi}\int_0^{2\pi}\ln 2[CC_1C_0C_0'+SS_1S_0S_0'+1 \\ -S_0S_0'\cos(\omega_1+\omega_2)-SS_1\cos(\omega_1-\omega_2)-(SS_0+S_1S_0')\cos\omega_1 \\ -(SS_0'+S_1S_0)\cos\omega_2]\,d\omega_1\,d\omega_2 \qquad (137)$$

Fig. 34

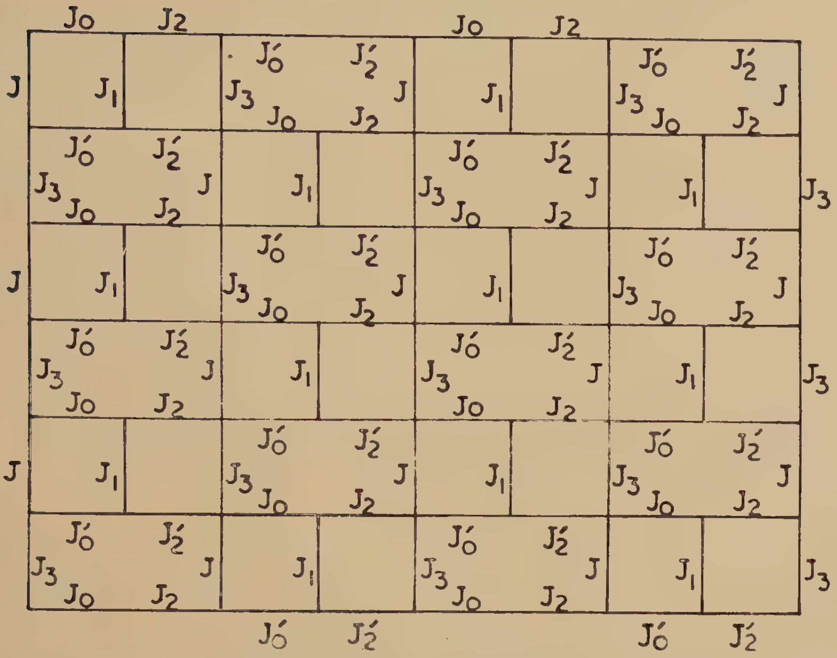


The chequer lattice with $\nu=0$ gives rise to the quadratic ($J=J_1$, $J_0=J_0'$), honeycomb ($J=0$), and triangular ($J=\infty$) lattices.

where n_∞ is the number of bond strengths J, J_1, J_0, J_0' which become infinite, the corresponding linked spins being regarded as one. A similar formula was given by Utiyama for general ν. As a particular example, the partition function for the kagomé lattice is given by

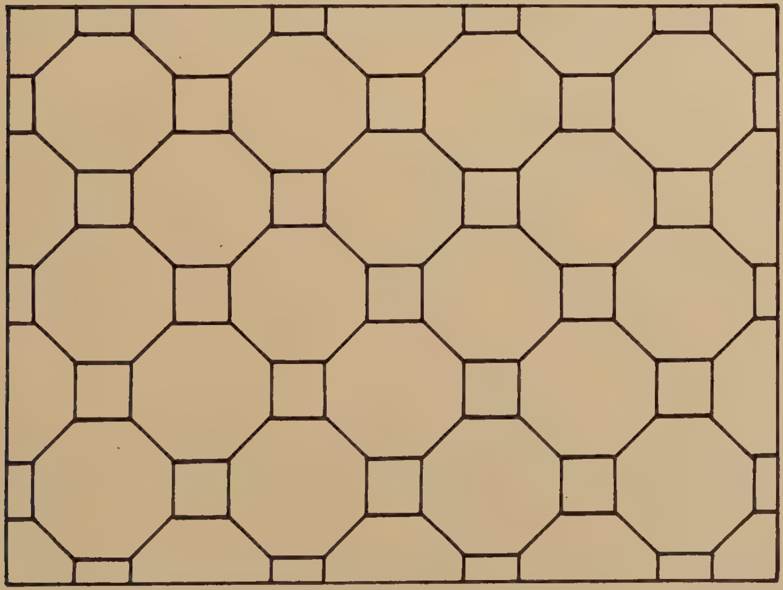
$$\ln(\lambda/2)=(24\pi^2)^{-1}\int_0^{2\pi}\int_0^{2\pi}\ln\tfrac{1}{4}\{C^6+S^6+2C^3S^3+3C^2-2(CS^3+C^2S^2) \\ \times[\cos\omega_1+\cos\omega_2+\cos(\omega_1+\omega_2)]\}\,d\omega_1 d\omega_2. \quad . \quad . \quad . \quad (138)$$

Fig. 35



The chequer lattice with $\nu=1$ gives rise to the kagomé lattice ($J=\infty$) and the 4–8 lattice ($J_3=0$).

Fig. 36



The 4–8 lattice. All vertices are equivalent but bonds belong to two groups, square and octagonal.

The approach of Utiyama indicated that the general formulae (59), (133), (134) apply only to lattices corresponding to $\nu=0$; they break down for the kagomé lattice for which $\nu=1$. The formula (133) of Onsager which determines the Curie point was also generalized to all lattices with $\nu=0$ in the form

$$\operatorname{gd} 2K+\operatorname{gd} 2K_1+\operatorname{gd} 2K_0+\operatorname{gd} 2K_0'=\pi. \quad . \quad . \quad . \quad . \quad (139)$$

Using the above approach and the duality, decoration, and star-triangle transformations, Syozi (1955 b) determined the Curie points of many complex lattices, some of them having average coordination number 5. By increasing the number of decorating spins it was possible to loosen the coordination of the lattice until the Curie point ultimately tended to $T=0$.

We may conclude generally that the mathematical nature of the singularities is the same for all of the two-dimensional lattices considered, and that the detailed thermodynamic properties of the model are very insensitive to change in lattice type.

3.6. *Exact Series Expansions*

All the results which we have derived so far correspond to two-dimensional lattices in the absence of a magnetic field. By applying certain transformations to the Onsager solution Fisher (1960) has derived an exact solution for an antiferromagnetic in a magnetic field; this corresponds to a specialized model, and we will defer consideration of its detailed properties to a subsequent publication. The methods described so far in this chapter are inapplicable in the presence of a magnetic field or in three dimensions. The most important source of exact information regarding the latter problems are series expansions of the partition function at low and high temperatures.

The derivation of substantial numbers of terms of these series gives rise to topological questions which will be considered in detail in § 5. Our present purpose is to formulate the problem, and establish the form of the expansions in different regions of the (μ, z) plane. We shall also find that an investigation of the propagation of order, and of the presence or absence of long-range order, will help us to identify the singularities of the partition function.

3.6.1. *Low temperature expansions*

We have already noted (§ 3.4.2) that at low temperatures the partition function can be expanded in terms of successive deviations (corresponding to more and more overturned spins) from the lowest energy state. Let us consider a set of N interacting spins ($J>0$) in a magnetic field in direction 2. (It is more useful in this case to derive a low density expansion.) Following the discussion and notation of § 2.2, the lowest energy state consists of all spins pointing in direction 2; there are ${}^NC_1$ excited states corresponding to one overturned spin, ${}^NC_2$ corresponding to two overturned spins, . . . ${}^NC_r$

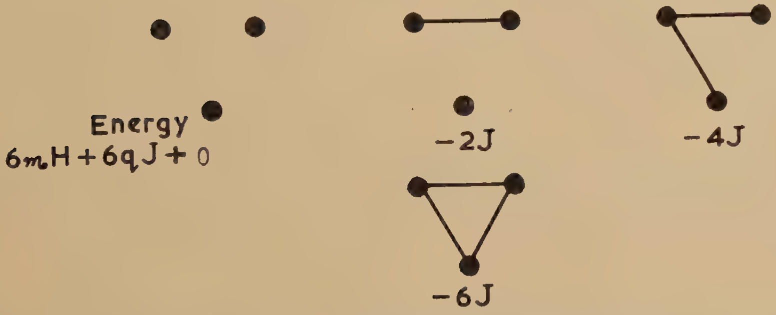
corresponding to r overturned spins. The ${}^{N}C_r$ spins can be divided into different energy groups; the highest energy deviation from the ground state, $(2rmH+2qrJ)$, arises from r spins, no two of which are nearest neighbours; the next from r spins with one nearest neighbour link, the next from r spins with two nearest neighbour links, and so on. Each nearest neighbour link decreases the energy by $2J$; as an example the configurations which correspond to $r=3$ are shown diagrammatically in fig. 37. We may thus expand $\Lambda_N(\mu, z)$ in the form

$$\Lambda_N(\mu,z)=1+\mu F_1(N,z)+\mu^2F_2(N,z)+\ldots\mu^rF_r(N,z)+\ldots(\mu<1) \quad (140)$$

where there are ${}^{N}C_r$ terms contributing to $F_r(N, z)$. For a simple quadratic lattice wrapped on a torus it is easy to see that

$$\left.\begin{aligned} &F_1(N,z)=Nz^4, \quad F_2(N,z)=2Nz^6+\frac{N(N-5)}{2\,!}z^8, \\ &F_3(N,z)=6Nz^8+2N(N-8)z^{10}+\frac{N^3-15N^2+62N}{6}z^{12}. \end{aligned}\right\} \quad . \quad (141)$$

Fig. 37



Low temperature configurations with three spins.

So far the expansion has been exact. We shall now allow N to become large and derive a corresponding expansion for $\Lambda(\mu, z)$. We shall first deduce certain relations formally, and will subsequently discuss the detailed justification. For large N we should expect on physical grounds that

$$\Lambda_N(\mu,z)\sim[\Lambda(\mu,z)]^N; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (142)$$

there might be a multiplying factor whose effect would become negligible for large N. Hence if we assume that $\Lambda(\mu, z)$ can be expanded as a power series in μ of the form

$$\Lambda(\mu,z)=1+\mu f_1(z)+\mu^2f_2(z)+\ldots\mu^rf_r(z)+\ldots \quad (\mu<1) \quad . \quad (143)$$

we can equate successive powers of N, and deduce the values of the $f_r(z)$ from the $F_r(N,z)$. In fact, for a lattice in which the edges are connected cyclically, there are no surface effects, and it will be found that the multiplying factor is unity. We then have an identity

$$\begin{aligned}1+\mu F_1(N,z)+\mu^2F_2(N,z)+\ldots\mu^rF_r(N,z)+\ldots\\ =1+{}^NC_1[\mu f_1(z)+\mu^2f_2(z)+\ldots\mu^rf_r(z)+\ldots]\\ +{}^NC_2[\mu f_1(z)+\mu^2f_2(z)+\ldots\mu^rf_r(z)+\ldots]^2\\ +\ldots{}^NC_s[\mu f_1(z)+\ldots\mu^rf_r(z)+\ldots]^s+\ldots.\end{aligned} \quad . \quad . \quad . \quad . \quad (144)$$

Putting $N=1$, we find the very simple relation

$$f_r(z)=F_r(1,z). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (145)$$

(Hence for the S.Q. lattice

$$f_1(z)=z^4, \quad f_2(z)=2z^6-2z^8, \quad f_3(z)=6z^8-14z^{10}+8z^{12}).$$

The derivation of this result depends on the identity of both sides of (144) and to convince oneself of its correctness it is advisable to write out fully the first few terms of each side of (144) in order to verify that this is an identity.

It is sometimes more convenient to use the expansion for $\ln\Lambda(\mu,z)$ in the form

$$\ln\Lambda(\mu,z)=\mu g_1(z)+\mu^2g_2(z)+\ldots\mu^rg_r(z)+\ldots, \quad (\mu<1) \quad . \quad . \quad . \quad (146)$$

the $g_r(z)$ being closely related to the cluster integrals in the Mayer theory (see § 4.5 for further details). If we take the exponential of (146) we can relate $g_r(z)$ to $F_r(N,z)$; expanding $F_r(N,z)$ in powers of N, we can write

$$F_r(N,z)=a_{rr}(z)N^r+a_{r(r-1)}(z)N^{r-1}+\ldots a_{r1}(z)N. \quad . \quad . \quad (147)$$

We now formally expand exp $[N\ln\Lambda(\mu,z)]$ in powers of the variable N and equate coefficients of powers of N; we deduce that

$$g_r(z)=a_{r1}(z), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (148)$$

that is $g_r(z)$ is the coefficient of N in the expansion of $F_r(N,z)$ in powers of N. (Thus for the S.Q. lattice

$$g_1(z)=z^4, \quad g_2(z)=2z^6-\tfrac{5}{2}z^8 \quad g_3(z)=6z^8-16z^{10}+10\tfrac{1}{3}z^{12}).$$

The justification for the results obtained above lies in the consideration of the form of $F_r(N,z)$ for increasing values of r/N. When the concentration of overturned spins is small it will be rare to find any doublets (pairs of adjacent overturned spins), and a treatment which considers only singlets will provide a reasonable approximation. Choosing $f_1(z)$ to satisfy (145), and ignoring all higher terms of the series (143), corresponds to taking

$$F_r(N,z)={}^NC_r[f_1(z)]^r, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (149)$$

and hence to neglecting doublets in $F_r(N,z)$. Similarly stopping the series after two terms corresponds to taking account correctly of doublet formation in $F_r(N,z)$ but not of higher clusters. Hence we see that the higher terms become significant as r/N increases, and can be dealt with in the same manner.

The argument is similar to that used by Mayer in the derivation of his cluster integral expansion (Mayer and Mayer 1940). For large N the series for $\Lambda_N(\mu, z)$ can be replaced by its maximum term; the evaluation of this maximum term as a function of μ and z would lead to relations equivalent to (142), (145) and (148).

We have so far ignored states in which more than half of the spins of the assembly point in direction 1, and in the presence of a magnetic field, however small, this is certainly valid for large N. When the field is zero these states become significant; we can easily take account of them because of the symmetry between directions 1 and 2, and we can write instead of (140)

$$\Lambda_N(\mu, z) = (1+\mu^N) + (\mu+\mu^{N-1})F_1(N, z) + (\mu^2+\mu^{N-2})F_2(N, z) + \ldots \\ + (\mu^r+\mu^{N-r})F_r(N, z) + \ldots, \quad \text{(for all } \mu). \qquad (150)$$

It will be verified that the relation (28) is now satisfied by $\Lambda_N(\mu, z)$. When μ is less than 1 the second term in each bracket of (150) is negligible and we recover (140).

When $\mu = 1$, both terms in each bracket are equal, and the expression (140) must be multiplied by a factor 2. On taking the Nth root, the expression (143) for $\Lambda(\mu, z)$ must be multiplied by $2^{1/N}$, and this differs negligibly from unity for large N. Hence $\Lambda(\mu, z)$ is continuous at $\mu = 1$.

The magnetization is given by

$$I_N = kT\frac{\partial}{\partial H}\ln Z_N = m\left[N - 2\mu\frac{\partial}{\partial\mu}\ln\Lambda_N(\mu, z)\right]. \qquad (151)$$

When $\mu = 1$, it will be seen from (150) that $\partial\Lambda_N/\partial\mu$ is equal to $N\Lambda_N$, and hence that $I = 0$. When $\mu < 1$, however, if we use the expansion (146), the magnetization is equal to

$$Nm\{1 - 2[\mu g_1(z) + 2\mu^2 g_2(z) + \ldots r\mu^r g_r(z) + \ldots]\}, \qquad (152)$$

and, as long as the expansion exists at $\mu = 1$ for sufficiently small z, this tends to a non-zero value as $\mu \to 1$. Hence there is a spontaneous magnetization for sufficiently small z. The existence of a spontaneous magnetization therefore depends on the possibility of a valid expansion of the type (146) for $\mu = 1$ near $z = 0$. For a one-dimensional chain every $f_r(z)$ starts with z^2, since any number of spins can be overturned with only two adjacent 1–2 links; hence the coefficients of z^2 in the expansions (143), (146) become infinite when $\mu = 1$ and there is no spontaneous magnetization. Similarly for a strip of any finite width, since a finite number of overturned spins can divide the chain into two parts, one of the coefficients in the expansion would become infinite. It is only when the model extends to infinity in two or more dimensions that high powers of μ necessitate correspondingly high powers of z, the expansions (143), (146) are valid when $\mu = 1$, and there is a spontaneous magnetization.

The above discussion is not put forward rigorously but to enable one to understand physically how the discontinuities in magnetization arise for the Ising model.

In the antiferromagnetic case ($J<0$) the expansions (143), (146) are still valid for fields sufficiently large compared with the coupling between spins. For small fields the same method can be used to derive a low temperature expansion for lattices which can be decomposed into two equivalent sublattices (§ 2.2). When considering the configurations which correspond to overturned spins (fig. 37) we must now differentiate between the two sublattices, and the problem is therefore more complicated. By analogy with § 2 (9) we write the partition function in the form

$$Z_N{}^I = y^{-qN/4}\Lambda_N{}^{(a)}(\mu, y), \quad [y = z^{-1} = \exp(2J/kT)] \quad . \quad . \quad (153)$$

and $\Lambda^{(a)}(\mu, y)$ can be expanded as a power series in y. For example, the first few terms of this expansion for the S.Q. lattice are (Brooks and Domb 1951)

$$\begin{aligned}\Lambda^{(a)}(\mu, y) = 1 + \tfrac{1}{2}(\mu^{-1}+\mu)y^4 + 2y^6 \\ + [-(\mu^{-2}+\mu^2)/8 + 3(\mu^{-1}+\mu) - \tfrac{3}{4}]y^8 + \ldots \quad (154)\end{aligned}$$

There are no discontinuities in $\Lambda^{(a)}(\mu, y)$ as $\mu \to 1$, and there is no spontaneous magnetization. As might be expected physically the singularities in an antiferromagnetic occur in the neighbourhood of the critical field, and are caused by the transition from the state of alternating order, represented by (154), to the state of lined-up spins represented by (143).

3.6.2. *High temperature expansions*

We have already noted in § 3.4.1 that eqns. (31), (32) and (33) provide a basis for expansions of the partition function in powers of $\tanh K$, i.e. high temperature expansions. Expansions of this kind were used by Kirkwood (1938) in considering order–disorder transitions, and by Opechowski (1937) for the Heisenberg model; they were further developed by van der Waerden (1941), Kramers and Wannier (1941), Oguchi (1949), Wakefield (1951), Sykes (1956) and others.

The detailed discussion is closely analogous to that of the previous section with line configurations replacing spin configurations, and $\mathcal{N}$ replacing N (fig. 6). We must sum every configuration over the σ_i variables; any one of the σ_i which does not occur explicitly in a term of the expansion (33) gives rise to a factor $(\mu^{-1/2}+\mu^{1/2})$ in this term; likewise any σ_i which occurs to an even power. Any σ_i which occurs to an odd power gives rise to a factor $(\mu^{-1/2}-\mu^{1/2})$. Thus we may write

$$\left.\begin{aligned}Z_N{}^I = (\mu^{-1/2}+\mu^{1/2})^N(\cosh K)^{\mathcal{N}}[1 + \tanh K\ \Phi_1(\mathcal{N}, \tau) + \\ + \tanh^2 K\ \Phi_2(\mathcal{N}, \tau) + \ldots \tanh^r K\ \Phi_r(\mathcal{N}, \tau) + \ldots], \\ \tau = (1-\mu)/(1+\mu).\end{aligned}\right\} . \quad (155)$$

Putting $\mathcal{N} = qN/2$, and comparing with (140), we derive an expansion for the partition function per spin in the form

$$\begin{aligned}Z = (\mu^{-1/2}+\mu^{1/2})(\cosh K)^{q/2}[1 + \tanh K\ \phi_1(\tau) + \tanh^2 K\ \phi_2(\tau) \\ + \ldots \tanh^r K\ \phi_r(\tau) + \ldots] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (156)\end{aligned}$$

where, following (145)

$$\phi_r(\tau) = \Phi_r(q/2, \tau). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (157)$$

This expansion is valid for all μ, and has smooth analytic behaviour at $\mu=1$, the magnetization being zero on this line. It is also applicable to antiferromagnetism ($K<0$).

High temperature expansions can also be thought of as arising from the moments of $g(N;\,N_1,N_{12})$ regarded as a probability distribution. We have from § 2 (5) and (9)

$$\left.\begin{aligned}\Lambda_N(\mu,z)&=\sum_{N_1,\,N_{12}} g(N;\,N_1,N_{12})\mu^{N_1}z^{N_{12}}\\ \text{where}\qquad z^{N_{12}}&=\exp(-2N_{12}K)=\sum_{s=0}^{\infty}(-1)^s\frac{N_{12}{}^s(2K)^s}{s\,!},\\ \mu^{N_1}&=\exp(-2N_1L)=\sum_{t=0}^{\infty}(-1)^t\frac{N_1{}^t(2L)^t}{t\,!}\,(L=mH/kT)\end{aligned}\right\}\qquad(158)$$

Hence we can write

$$\Lambda_N(\mu,z)=\sum_{s,\,t=0}^{\infty}(-1)^{s+t}\frac{\langle N_{12}{}^sN_1{}^t\rangle(2K)^s(2L)^t}{s\,!\,t\,!},\qquad(159)$$

and $\Lambda_N(\mu,z)$ is the moment generating function for a completely random mixture. The properties of a random mixture for a simple quadratic lattice are of statistical interest in relation to the infection of trees in an orchard and were considered by Moran (1947). He calculated several moments, and proved that the distribution is normal for large N. The latter result is not surprising physically, and tells us that

$$\ln\Lambda_N(\mu,z)\sim N\ln\Lambda(\mu,z)$$

for large N; for detailed knowledge of the partition function and its singularities we require exact values of all the cumulants of the distribution.

3.6.3. *Fluctuations*

The expansion discussed in § 3.6.1 divides the partition function into terms corresponding to various possible configurations of the assembly, and by Boltzmann's principle each term is proportional to the probability of achieving the corresponding configuration; thus from (150) the probability of exactly r spins pointing in direction 1 is $\mu^rF_r(N,z)/\Lambda_N(\mu,z)$. Hence the mean number of spins pointing in direction 1 is given by

$$\begin{aligned}\langle N_1\rangle\Lambda_N(\mu,z)&=N\mu^N+[\mu+(N-1)\mu^{N-1}]F_1(N,z)\\&\quad+\ldots[r\mu^r+(N-r)\mu^{N-r}]F_r(N,z)+\ldots.\end{aligned}\qquad(160)$$

When $\mu<1$ the second term in each factor on the right-hand side can be neglected, and

$$\begin{aligned}\Lambda_N\langle N_1\rangle&=\mu\,\partial\Lambda_N/\partial\mu\simeq N\mu\Lambda^{N-1}\,\partial\Lambda/\partial\mu.\\ \langle N_1\rangle&\simeq N\mu\Lambda_\mu/\Lambda.\end{aligned}\qquad(161)$$

However when $\mu=1$, $\langle N_1\rangle=N/2$, and there is a discontinuity in $\langle N_1\rangle$ at $\mu=1$.

Similarly $\langle N_1{}^s \rangle$ is determined by $(\mu\,\partial/\partial\mu)^s \Lambda_N(\mu, z)$. When $\mu < 1$ the mean square deviation is given by

$$\langle N_1{}^2 \rangle - \langle N_1 \rangle^2 \simeq N[\mu^2 \Lambda_{\mu\mu}/\Lambda + \mu\Lambda_\mu/\Lambda - (\mu\Lambda_\mu/\Lambda)^2], \quad . \quad (162)$$

and the fluctuations are normal. But when $\mu = 1$ we obtain instead

$$\langle N_1{}^2 \rangle - \langle N_1 \rangle^2 \simeq \frac{N^2}{4}[1 - 2\theta(z)]^2 + N[\delta(z) + \theta(z) - \theta(z)^2], \quad . \quad (163)$$

where $\theta(z) = \underset{\mu\to1}{\mathrm{Lt}}\ \mu\Lambda_\mu/\Lambda$, $\delta(z) = \underset{\mu\to1}{\mathrm{Lt}}\ \mu^2\Lambda_{\mu\mu}/\Lambda$. Therefore, as long as θ is less than half the fluctuations in N_1 are greater than normal, the r.m.s. deviations being of order N. Fluctuations in N_{12} can be determined by differentiating partially with respect to z instead of μ; the results can also be confirmed from eqn. (159).

3.6.4. *Expansions for the degree of order*

The methods of the previous sections can be used to provide expansions at high and low temperatures of the degree of order discussed in § 3.3 (Oguchi 1951). At high temperatures we have already defined the appropriate configurational problem for the quadratic net in (125), and this can readily be extended to other cases. We have the corresponding general relation for the correlation beween spins a and b

$$Z_N{}^I \langle \sigma_a \sigma_b \rangle = \cosh^{\mathscr{N}} K \prod_{i,j} \sigma_a \sigma_b (1 + \sigma_i \sigma_j \tanh K) \prod_i \exp \frac{mH}{kT} \sigma_i, \qquad (164)$$

the detailed expansion of which can be undertaken in the same manner as (155). The first term in the expansion, arising from no lines, will give rise to a term τ^2; this is equal to $\langle \sigma_a \rangle \langle \sigma_b \rangle$ to the first order, and corresponds to the absence of correlation at sufficiently high temperatures. Correlation is introduced by line configurations (e.g. fig. 6), and $\mathscr{S}_{ab}$ can be determined from (19).

At low temperatures, for a ferromagnetic in a magnetic field, we can determine $\langle \alpha_{11}{}^{ab} \rangle$ (§ 3.3) by a method similar to that of § 3.6.3. Let $F_r{}^{ab}(N, z)$ represent the sub-group of $F_r(N, z)$ in which spins a and b are both overturned. Then

$$\Lambda_N(\mu, z) \langle \alpha_{11}{}^{ab} \rangle = \mu^2 F_2{}^{ab}(N, z) + \mu^3 F_3{}^{ab}(N, z) + \ldots \mu^r F_r{}^{ab}(N, z) + \ldots . \quad . \quad . \quad . \quad . \quad (165)$$

$\langle \alpha_1 \rangle$ is equal to $\langle N_1 \rangle / N$ and is therefore determined by (161). Hence we can calculate $\mathscr{S}_{ab}$ from (18). In the presence of a magnetic field there is only one lowest energy state; correlation between the specified spins arises only from configurations with continuous chains of overturned spins containing both specified spins. If the two specified spins are sufficiently far apart no such configurations enter, $\langle \alpha_{11}{}^\infty \rangle = \langle \alpha_1 \rangle^2$ and $\mathscr{S}_\infty = 0$.

In the absence of a magnetic field, however, both of the equivalent lowest energy states must be taken into account. If the lowest energy state at absolute zero consists of all spins pointing in direction 2, the mean fraction of spins pointing in direction 1 at any temperature is equal to $\theta(z)$, from (161) and (163); the mean fraction pointing in direction 2 is $[1-\theta(z)]$. Thus since both lowest energy states are equally probable,

$$\langle\alpha_{11}{}^{\infty}\rangle=\tfrac{1}{2}[\theta(z)]^2+\tfrac{1}{2}[1-\theta(z)]^2=\tfrac{1}{2}[1-2\theta(z)+2\theta(z)^2]. \tag{166}$$

$\langle\alpha_1\rangle$ is equal to $\frac{1}{2}$, and hence from (18)

$$\langle\alpha_{11}{}^{\infty}\rangle=\tfrac{1}{4}(1+\mathscr{S}_{\infty})=\tfrac{1}{4}(1+R^2). \tag{167}$$

Thus we deduce that

$$R=1-2\theta, \tag{168}$$

i.e. that the long-range order is equal to the spontaneous magnetization. We see also that long-range order arises physically as a result of the interference of equivalent lowest energy configurations.

For an antiferromagnetic in the absence of a magnetic field the result (168) remains valid, although there is now no spontaneous magnetization. But in the presence of a magnetic field a new calculation is required since long-range order is present for all magnetic fields of magnitude less than a critical value. We are concerned with lattices which can be sub-divided into two equivalent sub-lattices, so that the lowest energy antiferromagnetic state corresponds to the spins of the sub-lattices all pointing in directions 1 and 2 respectively. These sub-lattices can be interchanged without affecting the energy, and the lowest energy level is therefore degenerate; this last result is true in the presence of a magnetic field, provided that the field is not sufficiently large to break the coupling between the spins and line them up (§ 2.2, § 2, fig. 2). Suppose that the field points in direction 2, and at any temperature T let $\langle\eta_1\rangle$ be the mean fraction of spins of sub-lattice 2 which are turned over from direction 2 to direction 1, and $\langle\eta_2\rangle$ the mean fraction of spins of sub-lattice 1 which have turned over from direction 1 to direction 2. Then

$$\langle\alpha_1\rangle=\tfrac{1}{2}(1+\langle\eta_1\rangle-\langle\eta_2\rangle). \tag{169}$$

To evaluate $\langle\alpha_{11}{}^{\infty}\rangle$ we must, as before, take equal account of both lowest energy states, and we find

$$\langle\alpha_{11}{}^{\infty}\rangle=\tfrac{1}{2}(1-\langle\eta_2\rangle)^2+\tfrac{1}{2}\langle\eta_1\rangle^2. \tag{170}$$

Hence from (18) we deduce that

$$R=\frac{1-\langle\eta_1\rangle-\langle\eta_2\rangle}{1+\langle\eta_1\rangle-\langle\eta_2\rangle}=1-\frac{2\langle\eta_1\rangle}{1+\langle\eta_1\rangle-\langle\eta_2\rangle}. \tag{171}$$

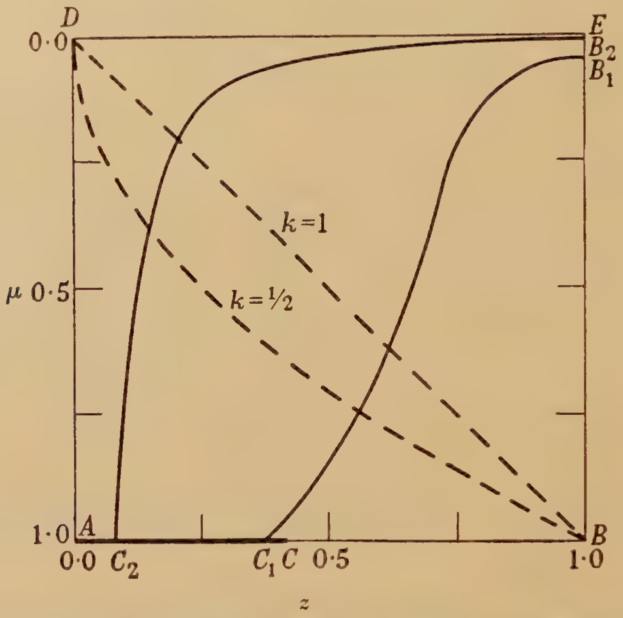
In the absence of a magnetic field both $\langle\eta_1\rangle$ and $\langle\eta_2\rangle$ are equal to $\theta(z)$, and we recover (168). It is interesting to note in the general case that R becomes zero when $\langle\eta_1\rangle+\langle\eta_2\rangle=1$, i.e. when on the average half of the spins in the lattice have overturned.

3.7. *Location of Singularities*

Having derived various types of series expansion, and specified the conditions of occurrence of long-range order, we are now in a position to outline the singularities of the partition function in the (μ, z) plane. These singularities are associated with the disappearance of long-range order.

Quite generally if we have established the existence of long-range order in an assembly for a finite temperature range above $T=0$, we know that a singularity must occur at a temperature T_c at which the long-range order becomes zero (for when the long-range order is non-zero it can be used to specify the temperature, and the assembly possesses an additional thermodynamic variable). For one-dimensional assemblies the long-range order which exists at $T=0$ disappears at a finite temperature however small.

Fig. 38



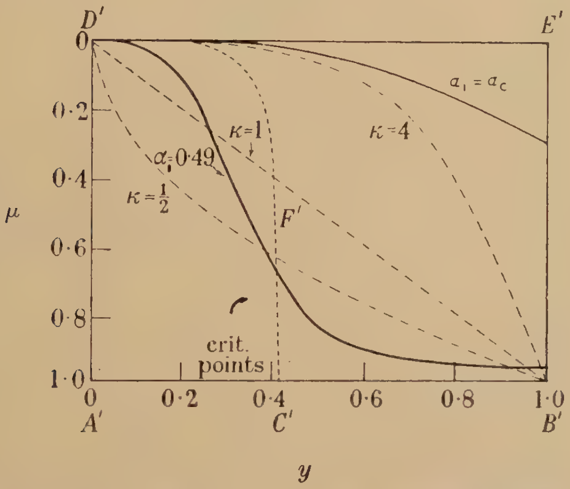
The singularities of the Ising model of a ferromagnetic. All singularities lie on AC. In the region $\mu<1$ there is no long-range order.

Let us first consider a ferromagnetic (Domb 1949 b). We need only deal with the range $0 \leqslant \mu$, $z \leqslant 1$, and this is illustrated in fig. 38. We know that in the range $\mu<1$ there is no long-range order, and in fact long-range order exists only when $\mu=1$, and at temperatures below the Curie point represented by C. Thus the only ordered region in the plane is the line AC. There is a discontinuity in Λ_μ as $\mu \to 1$ for $z<z_c$.

The low density expansion represented by (143) corresponds to starting at some point of DE and moving parallel to DA. The low temperature expansion when $\mu=1$ corresponds to starting at A and moving along AC. The high temperature expansion (156) corresponds to starting at some point of BE and moving parallel to BA. From our discussion we should expect the partition function to have no singularities except on the line $\mu=1$; this was established rigorously by Yang and Lee (1952), who considered very generally the conditions which give rise to singularities in cooperative assemblies. In the presence of a finite magnetic field, therefore, the thermodynamic functions behave smoothly and analytically. We shall also find that the two expansions (143) and (156), which we derived by independent methods, are closely related and can be deduced from one another.

The antiferromagnetic corresponds to the range $1 \leqslant z \leqslant \infty$ but we shall prefer to use the variable $y = z^{-1}$, so that again $0 \leqslant \mu, y \leqslant 1$ (fig. 39). For a lattice which can be sub-divided into equivalent sub-lattices the solution when $\mu = 1$, represented by A′B′, is identical with that for a ferromagnetic, the Curie point being at C′. There is now no spontaneous magnetization as $\mu \rightarrow 1$, and the partition function behaves smoothly and analytically in this region. However, the long-range order which is present along A′C persists in the presence of a magnetic field, and the points in the (μ, y) plane at which it disappears trace out a curve of singularities D′F′C′ dividing ordered from disordered states. At low temperatures we should expect this curve to correspond to the critical field (§ 2.2), and hence to be given by $\mu = K_0 y^4$ where K_0 is a constant. In the disordered region the expansion (156) remains valid starting from a point on B′E′ and moving parallel to B′C′, and the expansion (143) starting at a point on D′E′ and moving parallel to D′A′. In the ordered region the expansion (154) can be used starting at points on A′D′ or A′C′. There are so far no general theorems for an antiferromagnetic of the type enunciated by Yang and Lee for a ferromagnetic; however, it seems reasonable to assume that the demarcation of singularities given here is valid.

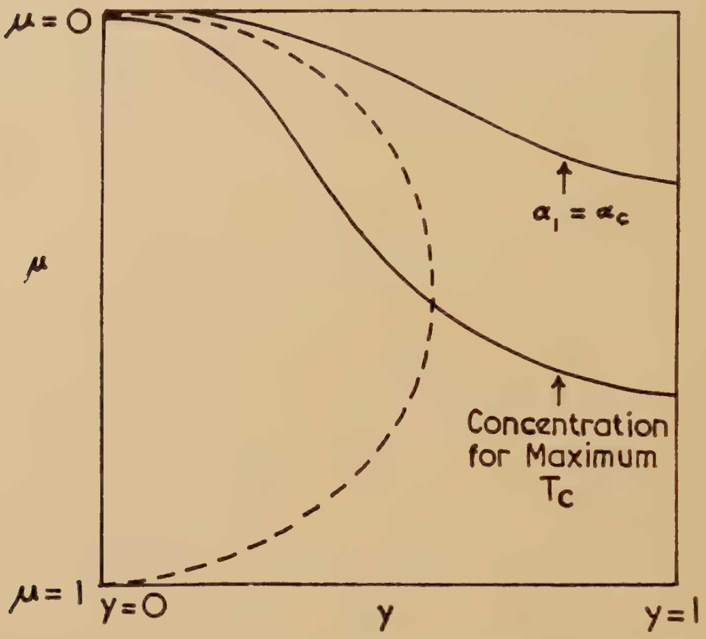
Fig. 39



The singularities of the Ising model of an antiferromagnetic. The line of singularities separates the region with long-range order from that with no long-range order.

For lattices such as the triangular there is no ordered state in the absence of a magnetic field. However, it is easy to see that when the ratio of positive to negative spins is 2 to 1 an ordered state can be constructed, and there will be an appropriate critical field for this ordered state. Hence it seems very probable that the singularities are as indicated in fig. 40.

Fig. 40



Singularities of the antiferromagnetic triangular lattice. In zero field there is no long-range order. In the presence of a magnetic field long-range order can exist.

3.7.1. *Application to regular solutions*

We have seen from § 2.3 that the thermodynamic properties of regular solutions are completely determined by the function $\Lambda(\mu, z)$. We shall now show how to interpret the singularities for the theory of regular solutions. From § 2.3 (10)—(13) the free energy for a solution of concentration α_1 is given by

$$F^S = -kT[\ln\Lambda - \alpha_1 \ln\mu] + q\alpha_1\epsilon_{11}/2 + q(1-\alpha_1)\,\epsilon_{22})/2 \quad . \quad . \quad . \quad (172)$$

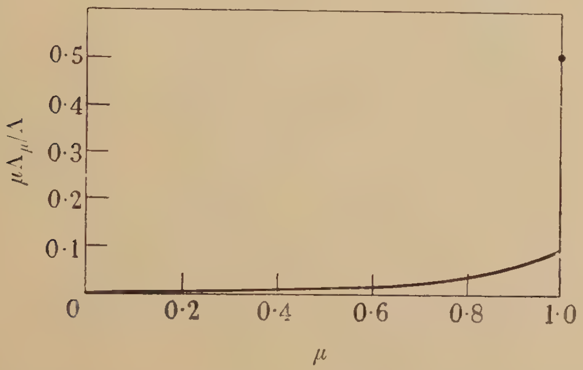
where

$$\mu\Lambda_\mu/\Lambda = \alpha_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (173)$$

The relation (173) determines a path in the (μ, z) plane along which Λ must be evaluated to determine F^S. When $\alpha_1 = \frac{1}{2}$ the path is AB (fig. 38). When α_1 is different from $\frac{1}{2}$ a different type of path results. For $z < z_c$ the general behaviour of $\mu\Lambda_\mu/\Lambda$ as a function of μ is similar to the curve in fig. 41. Its value increases steadily from zero at $\mu = 0$ to $\theta(z)$ at $\mu = 1$ and there is a jump to $\frac{1}{2}$ at $\mu = 1$. This discontinuity arises for an infinite lattice, and would be a very rapid continuous change for a large finite lattice. Hence if $\theta(z) < \alpha_1 < \frac{1}{2}$ the relation (173) can only be satisfied on the line AB. For $z = 1$ we can use the high temperature expansion (156) to show that $\mu/(1+\mu) \to \alpha_1$. Thus for any value of α_1 different from $\frac{1}{2}$ the path given by (173) moves along AC until $\theta(z) = \alpha_1$, and then it turns into the plane cutting BE in a point $\mu = \alpha_1/(1-\alpha_1)$. Typical paths are AC_1B_1, AC_2B_2.

Clearly a transition takes place at points such as C_1, and we shall interpret the portion AC_1 as corresponding to a separation into two phases, and the portion C_1B_1 as solution. This interpretation is borne out by the curve of free energy as a function of concentration shown in fig. 42. (For simplicity the case $\epsilon_{11} = \epsilon_{22}$ has been taken, but the resulting features are essentially the same for the general case.) The portion AC_1 may be regarded as a mixture of two phases at Y, phase I being a solution of $\theta(z)$ of substance 1 in substance 2, and phase II a solution of $\theta(z)$ of substance 2 in substance 1. $\theta(z)$ is thus the maximum concentration which can exist in solution at the given temperature, and is in fact the solubility curve for the two substances. As we move along AC_1 the proportion of phase II gets smaller until at C_1 it disappears. The nature of the transition at C_1 can be shown to be second order (i.e. a simple discontinuity in specific heat) (Domb 1949); it is analogous to the transition in a liquid-vapour mixture at constant volume. For $\alpha_1 = \frac{1}{2}$ the transition takes place at C, the specific heat singularity being more complex. For a two-dimensional lattice it is a logarithmic infinity of the Onsager type.

Fig. 41

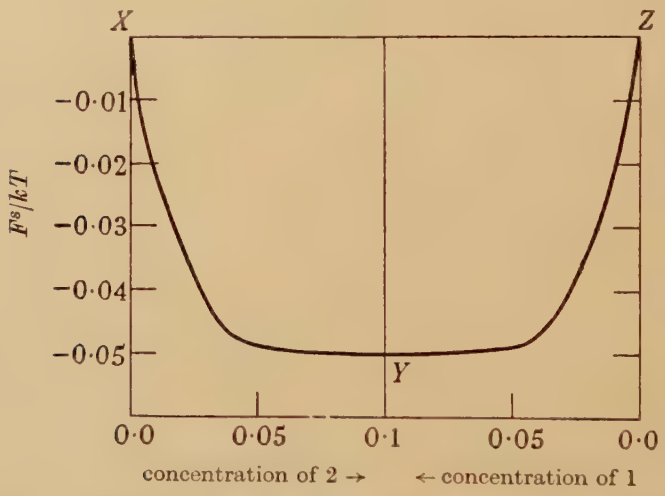


Discontinuous behaviour of Λ_μ at $\mu = 1$ for $T < T_c$. The function $\mu\Lambda_\mu$ increases steadily from 0 at $\mu = 0$ to $\theta(z)$ as $\mu \to 1$, then jumps discontinuously to $\frac{1}{2}$ at $\mu = 1$.

3.7.2. *Order–disorder transitions*

When the interaction energy in a regular solution favours the formation of a superlattice, the eqns. (172), (173) remain valid, but the singularities diagram for an antiferromagnetic is now relevant to the interpretation. When the lattice can be divided into two equivalent sub-lattices fig. 39 is appropriate. When $\alpha_1 = \frac{1}{2}$ the path is A′B′ as before; for $\alpha_1 < \frac{1}{2}$ a different type of path again results. Examination of the series (154) for the ordered region shows that the dominant terms as μ and y tend to zero are of the form $(\mu^{-1}y^q)^s$; similarly the dominant terms in the series (143) for the disordered region are of the form $(\mu z^q)^s = (\mu y^{-q})^s$. Hence in both cases the relation (173) can only be satisfied if μy^{-q} tends to a finite non-zero value as $y \to 0$. As $y \to 1$, $\mu/(1+\mu) \to \alpha_1$ as before.

Fig. 42



Free Energy VS concentration for a Solid Solution ($T < T_c$). For concentrations between 0·1 and 0·9 the free energy curve is a horizontal line, the assembly having separated into two phases.

Typical paths are drawn in fig. 39 for various values of α_1. It is clear that for sufficiently small α_1 the path lies completely within the region D′F′C′B′E′ in which no long-range order exists; the path does not cross the line of singularities D′F′C′ and no critical effects will be present. On the other hand, for values of α_1 near to $\frac{1}{2}$, the path lies within the region of long-range order A′D′F′C′ for sufficiently low temperatures, and crosses the line of singularities to pass into the region D′F′C′B′E′ as the temperature is raised; there is thus a singularity corresponding to the disappearance of long-range order. We deduce that a critical concentration, α_c, exists below which there is no long-range order even at the absolute zero, and above which there is a normal Curie point.

For lattices like the triangular and F.C.C. the singularities diagram is fig. 40. Again we should find a critical concentration, α_c, below which long-range order is absent. For $\alpha_1 > \alpha_c$ however, the Curie temperature increases to a maximum for a concentration $\alpha_m < \frac{1}{2}$, and then decreases to zero for $\alpha_1 = \frac{1}{2}$. The discussion of this case is somewhat more tentative because of the lack of an adequate series for the ordered region.

APPENDIX I

§1. THEOREM OF PERRON AND FROBENIUS FOR SYMMETRIC MATRICES

Let **V** be a symmetric matrix of order t with positive elements. The eigenvalues of **V** are all real, and with **V** we can associate a quadratic form which can be reduced to canonical form by a real orthogonal transformation. This quadratic form can therefore be written as

$$\lambda_1(\alpha_1 x_1 + \ldots + \alpha_t x_t)^2 + \lambda_2(\beta_1 x_1 + \ldots \beta_t x_t)^2 + \ldots + \lambda_t(\theta_1 x_1 + \ldots \theta_t x_t)^2,$$

and the $\alpha_i, \beta_i \ldots \theta_i$ form an orthogonal matrix, where the λ_i are taken in descending order of magnitude. We shall prove that if $\lambda_1 = \lambda_2$ ($=1$ for simplicity), and $\lambda_3, \ldots \lambda_t < 1$, the coefficients of the quadratic form cannot all be positive.

Consider the coefficient of $x_i x_j$ $(i \neq j)$. This is equal to

$$\alpha_i\alpha_j + \beta_i\beta_j + \lambda_3\gamma_i\gamma_j + \ldots \lambda_t\theta_i\theta_j$$
$$= (\lambda_3 - 1)\gamma_i\gamma_j + (\lambda_4 - 1)\delta_i\delta_j + \ldots + (\lambda_t - 1)\theta_i\theta_j, \qquad (174)$$

in view of the orthogonality condition. All the coefficients in the right-hand side of (174) are negative. Thus if we define

$$\gamma_i^* = \sqrt{(1-\lambda_3)}\gamma_i, \ldots, \quad \theta_i^* = \sqrt{(1-\lambda_t)}\theta_i,$$

these quantities may be regarded as components of t vectors in $(t-2)$ dimensional space, and the coefficient of $x_i x_j$ is minus the scalar product of the ith and jth vectors of this set. Our task is then to prove that if any t vectors are taken in $(t-2)$ dimensional space the angles between pairs of vectors cannot all be obtuse.

The theorem is elementary for $t = 4$. We shall prove the case $t = 5$ but the method can clearly be extended to any t, and is due to Dr. S. R. Tims (of King's College, London).

We can take the first vector ξ_1 to have coordinates $(a_1, 0, 0)$ $(a_1 > 0)$ and we shall introduce the remaining vectors one at a time ensuring at each stage that all the angles are obtuse. The second vector ξ_2 must have its first component negative, equal to $-a_2 (a_2 > 0)$; we choose the second coordinate axis in the plane of ξ_1, ξ_2 so that ξ_2 is $(-a_2, b_2, 0)$ $(b_2 > 0)$. Now the third vector ξ_3 makes an obtuse angle with both ξ_1 and ξ_2 and hence its first two components are negative; the third coordinate axis can now be chosen so that ξ_3 is $(-a_3, -b_3, c_3)(a_3, b_3, c_3 > 0)$. The remaining two vectors ξ_4 and ξ_5 must make obtuse angles with ξ_1, ξ_2 and ξ_3 and it will be seen that their coordinates are

$$(-a_4, -b_4, -c_4)\ (-a_5, -b_5, -c_5)\ (a_4, b_4, c_4, a_5, b_5, c_5 > 0).$$

Hence ξ_4 and ξ_5 must make an acute angle with each other.

The generalization to the case when more than 2 of the λ_i are equal is immediate. The case $\lambda_1 = 1$, $\lambda_2 = -1$ can be excluded since it would involve $\mathrm{Tr}\,(\mathbf{V}^r) \simeq 0$ or 2 for large r according as r is odd or even. It can readily be shown that this is impossible since all the elements of $\mathbf{V}^r$ are positive for all r.

APPENDIX II

§1. Exact Calculations of the Properties of Two-dimensional Lattices

1.1. *General Remarks*

We have seen in this chapter how the partition function of the Ising Model in zero magnetic field for certain two-dimensional lattices can be reduced to the evaluation of a double integral. The detailed reduction of this double integral and the derivation of the thermodynamic properties of different lattices is given in the literature, but it seemed worth assembling the results together for reference purposes. Also a number of unifying features emerge when the problems are treated collectively.

We shall be primarily concerned with isotropic interactions, in which all directions in the lattice are equivalent, and we shall deal with the quadratic, triangular, honeycomb, and kagomé lattices. The partition function for the quadratic lattice (94) is expressed in terms of the integral

$$\frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{2\pi} \ln(A_1 - B_1\cos\theta - B_1\cos\phi)\,d\theta\,d\phi, \quad . \quad . \quad . \quad (175)$$

where $A_1 = \cosh^2 2K$, $B_1 = \sinh 2K$.

It will be seen that $A_1 \geqslant 2B_1$ for all K, the equals sign occurring at the Curie point, and giving rise to a singularity in the integral at $\theta = \phi = 0$. Similarly the partition functions for the other three lattices (127), (131) and (138) are expressed in terms of the integral

$$\frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{2\pi} \ln[C_1 - D_1\cos\theta - D_1\cos\phi - D_1\cos(\theta+\phi)]\,\mathrm{d}\theta\,\mathrm{d}\phi. \quad (176)$$

where C_1 and D_1 have the following values:

Triangular:	$C_1 = \cosh^3 2K + \sinh^3 2K$,	$D_1 = \sinh 2K$;
Honeycomb:	$C_1 = 1 + \cosh^3 2K$,	$D_1 = \sinh^2 2K$;
Kagomé:	$C_1 = \frac{1}{4}[\cosh^6 2K + \sinh^6 2K + 2\cosh^3 2K \sinh^3 2K + 3\cosh^2 2K]$,	$D_1 = \frac{1}{2}(\cosh 2K \sinh^3 2K + \cosh^2 2K \sinh^2 2K)$.

Again $C_1 \geqslant 3D_1$ for all K, the equals sign occurring at the Curie point, and giving rise to a singularity in the integral at $\theta = \phi = 0$.

The integrals (175), (176) cannot be reduced to tabulated form, and for the purposes of transformation it is better to consider the internal energy, which involves the partial derivatives with respect to A_1 or C_1 of the above integrals. We therefore concentrate attention on the integrals:
Quadratic lattice:

$$I_1(\xi_1) = \frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{2\pi}\frac{d\theta\,d\phi}{\xi_1 - \cos\theta - \cos\phi}\,(\xi_1 = A_1/B_1). \quad . \quad . \quad (177)$$

Other lattices:

$$I_2(\eta_1) = \frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{2\pi}\frac{d\theta\,d\phi}{\eta_1 - \cos\theta - \cos\phi - \cos(\theta+\phi)}\,(\eta_1 = C_1/D_1). \quad (178)$$

Using the standard result

$$\frac{1}{2\pi}\int_0^{2\pi}\frac{d\psi}{\zeta - \cos\psi} = (\zeta^2 - 1)^{1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (179)$$

we can reduce both integrals (177), (178) to complete elliptic integrals of the first kind.

For (177), we apply (179) to one of the variables, and use the formula (Bateman Manuscript Project 1953, pp. 308, 309)

$$\left.\begin{aligned}\int_\delta^\gamma \frac{dx}{\sqrt{[(\alpha-x)(\beta-x)(\gamma-x)(x-\delta)]}} &= \frac{2\mathscr{K}\left\{\left(\sqrt{\dfrac{(\alpha-\beta)(\gamma-\delta)}{(\alpha-\gamma)(\beta-\delta)}}\right)\right\}}{\sqrt{[(\alpha-\gamma)(\beta-\delta)]}},\\ \mathscr{K}(k_1) &= \int_0^{\pi/2}(1-k_1^2\sin^2\psi)^{-1/2}\,d\psi.\end{aligned}\right\} \quad (180)$$

We find that

$$I_1(\xi_1) = \frac{2}{\pi\xi_1}\mathscr{K}(2/\xi_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (181)$$

For (178), we combine the terms $\cos\theta$ and $\cos(\theta+\phi)$ and integrate with respect to θ; we then apply (180) to the result and obtain

$$I_2(\eta_1) = \frac{2}{\pi}\frac{1}{[\frac{1}{4}(\nu_1^4 - 6\nu_1^2 - 3) + 2\nu_1]^{1/2}}\,\mathscr{K}\left[\frac{2}{1 + \frac{1}{8}(\nu_1^3 - 6\nu_1 - 3\nu_1^{-1})}\right]$$

$$(\nu_1 = 3 + 2^2\eta_1). \quad . \quad . \quad . \quad . \quad . \quad . \quad (182)$$

Hence we see that the energy and specific heat can be expressed in terms of complete elliptic integrals, but the free energy and entropy involve the integrals of these functions.

1.2. *Curie Points*

The Curie points of the lattices are readily determined by the transformations of §§ 3.4.2, 3.4.3, 3.4.4 and are as follows:

$$\left.\begin{array}{llll}\text{Quadratic:} & z_c = (\sqrt{2}-1) & = 0{\cdot}4142136, & kT_c/J = 2{\cdot}269185;\\ \text{Triangular:} & z_c = 1/\sqrt{3} & = 0{\cdot}5773503, & kT_c/J = 3{\cdot}640957;\\ \text{Honeycomb:} & z_c = (2-\sqrt{3}) & = 0{\cdot}2679492, & kT_c/J = 1{\cdot}518652;\\ \text{Kagomé:} & z_c = [(2/\sqrt{3})-1]^{1/2} & = 0{\cdot}3933198, & kT_c/J = 2{\cdot}143319.\end{array}\right\} \quad . \quad . \quad . \quad (183)$$

1.3. *Critical Constants*

The detailed formulae for the internal energy per spin are obtained from (94), (127), (131), (138) by differentiation in the usual manner, and are as follows:

$$\left.\begin{array}{ll}
\text{Quadratic:} & E/J=-\dot{B}_1/2B_1-\dot{\xi}_1 I_1(\xi_1)/2\,;\\
\text{Triangular:} & E/J=-\dot{D}_1/2D_1-\dot{\eta}_1 I_2(\eta_1)/2\,;\\
\text{Honeycomb:} & E/J=-\dot{D}_1/4D_1-\dot{\eta}_1 I_2(\eta_1)/4\,;\\
\text{Kagomé:} & E/J=-\dot{D}_1/6D_1-\dot{\eta}_1 I_2(\eta_1)/6.
\end{array}\right\} \quad . \quad . \tag{184}$$

Here the dot refers to differentiation with respect to K. At the Curie point we have pointed out that ξ_1 and η_1 have maxima, and their derivatives are consequently zero. Thus the critical values of the energy are determined by the first terms on the right-hand side of (184), and are expressible in terms of surds. They are as follows:

$$\left.\begin{array}{ll}
\text{Quadratic:} & E_c/J=-\sqrt{2}=-1{\cdot}414214\,;\\
\text{Triangular:} & E_c/J=-2\,;\\
\text{Honeycomb:} & E_c/J=-2/\sqrt{3}=-1{\cdot}154701\,;\\
\text{Kagomé:} & E_c/J=-(1+2\sqrt{3})/3=-1{\cdot}488034.
\end{array}\right\} \tag{185}$$

To determine the critical values of the entropy we shall first need the critical values of $\ln\lambda$. For the quadratic lattice this involves the numerical value of the definite integral

$$G_1=\frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{2\pi}\ln\left[1-\tfrac{1}{2}(\cos\theta+\cos\phi)\right]d\theta\,d\phi, \quad . \quad . \tag{186}$$

which can be related to Catalan's constant G

$$G_1=\frac{4}{\pi}G-2\ln 2=-0{\cdot}2200508 \quad . \quad . \quad . \quad . \quad . \tag{187}$$

(where $G=1^{-2}-3^{-2}+5^{-2}-7^{-2}+\ldots=0{\cdot}915\,965\,594$).
For the other three lattices the corresponding definite integral is

$$G_2=\frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{2\pi}\ln\{1-\tfrac{1}{3}[\cos\theta+\cos\phi+\cos(\theta+\phi)]\,d\theta\,d\phi, \tag{188}$$

which was evaluated numerically by Houtappel as $\simeq -0{\cdot}17642$. Hence we have for the critical values of $\ln\lambda$:

$$\left.\begin{array}{ll}
\text{Quadratic:} & \ln\lambda_c=\ln(z_c^{-1}+z_c)+\tfrac{1}{2}G_1=0{\cdot}929695\,;\\
\text{Triangular:} & \ln\lambda_c=\tfrac{1}{2}\ln(z_c^{-3}+3z_c)+\tfrac{1}{2}G_2=0{\cdot}87959\,;\\
\text{Honeycomb:} & \ln\lambda_c=\tfrac{1}{4}\ln[z_c^{-3}+z_c^{3}+3z_c^{-1}+3z_c+8]+\tfrac{1}{4}G_2=1{\cdot}02506\,;\\
\text{Kagomé:} & \ln\lambda_c=\tfrac{1}{6}\ln[z_c^{-6}+18z_c^{-2}+24+21z_c^{2}]+\tfrac{1}{6}G_2=0{\cdot}97479.
\end{array}\right\}$$

$$. \quad . \quad . \quad . \tag{189}$$

The corresponding values of the entropy are given by

$$S_{\mathrm{c}}/k = \ln \lambda_{\mathrm{c}} + E_{\mathrm{c}}/kT_{\mathrm{c}},$$

and are respectively

$$0{\cdot}30647,\ 0{\cdot}33028,\ 0{\cdot}26471,\ 0{\cdot}28052. \qquad \ldots \quad (190)$$

1.4. *Calculation of Thermodynamic Functions*

The internal energy, E, is given by (184), and substituting for the quadratic lattice, and using (181) we obtain

$$\left.\begin{aligned} E/J &= -\coth 2K \left[1 + \frac{2}{\pi} k_1'' \mathscr{K}(k_1) \right] \\ k_1 &= 2/\xi_1 = 2 \sinh 2K/\cosh^2 2K, \\ k_1'' &= 2 \tanh^2 2K - 1 = \pm (1 - k_1^2)^{1/2}. \end{aligned}\right\} \quad \ldots \quad (191)$$

The specific heat per spin is given by

$$\begin{aligned} C_{\mathrm{v}}/k &= -K^2 \frac{d}{dK}(E/J) \\ &= \frac{2}{\pi}(K \coth K)^2 \{2\mathscr{K}(k_1) - 2\mathscr{E}(k_1) - (1 - k_1'')[\tfrac{1}{2}\pi + k_1'' \mathscr{K}(k_1)]\} \end{aligned} \quad (192)$$

where

$$\mathscr{E}(k_1) = \int_0^{\pi/2} (1 - k_1^2 \sin^2 \psi)^{1/2} \, d\psi,$$

and we have used the relation (Edwards 1921, p. 399)

$$\int_0^{\pi/2} d\psi/(1 - k_1^2 \sin^2 \psi)^{3/2} = \mathscr{E}(k_1)/k_1'^2 \quad (k_1'^2 + k_1^2 = 1). \quad \ldots \quad (193)$$

The partition function can be obtained by integrating (177) with respect to A_1, using (181), and we readily establish the formula

$$\ln(\lambda/2 \cosh 2K) = \frac{1}{2\pi} \int_0^{\pi} \ln\{\tfrac{1}{2}[1 + (1 - k_1^2 \sin^2 \psi)^{1/2}]\} \, d\psi. \quad . \quad (194)$$

Although this integral cannot be expressed in closed form Onsager (1944) derived rapidly convergent series expansions. With the notation

$$k_1' = |k_1''|, \quad \ln q_1 = \pi \tau_1 i = -\pi \mathscr{K}(k_1')/\mathscr{K}(k_1),$$

one or other of the following expressions is suitable:

$$\begin{aligned} \ln \lambda &= \tfrac{1}{2} \ln(2 \sinh 2K) - \tfrac{1}{4} \ln q_1 + \sum_{r=1}^{\infty} (-1)^r (2r - 1) \ln(1 - q_1^{2r-1}), \\ \ln \lambda &= \tfrac{1}{2} \ln(2 \sinh 2K) + (2/\pi) G + \frac{1}{\pi} \sum_{r=0}^{\infty} (-1)^r \\ &\quad \times \frac{\{1 + (2r+1)(\pi i/\tau_1) - \exp[-(2r+1)\pi i/\tau_1]\}}{(2r+1)^2 \sinh^2[(r + \frac{1}{2})\pi i/\tau_1]}. \end{aligned} \quad \ldots \quad (195)$$

We have noted that k_1 is always $\leqslant 1$; temperatures above and below the Curie point correspond to the same value of k_1 since k_1 is invariant under the inversion transformation (§ 3.4.3). The internal energy for the other lattices can be obtained from (184), the appropriate η_1 being invariant under the corresponding inversion transformation. For the triangular lattice ν_1 of (182) takes on the simple value $1/vz$, and for the honeycomb lattice

$$1/v^*z^* = \left(\frac{1+v}{1-v}\right)\left(\frac{1+z}{1-z}\right)$$

in the notation of § 3.4.3. The specific heat can be obtained by differentiation, and the partition function by integration of (178) with respect to C_1.

It is interesting to note that the elliptic integrals in (181) and (182) can be reduced to forms in which the modulus is identical for quadratic, triangular and honeycomb lattices. Writing K_{inv} for the inverse temperature given by (43), (58) and (61) respectively, this modulus is

$$\kappa_1 = \frac{\sinh 2K_{\text{inv}}}{\sinh 2K} = \frac{v^{-1}-v}{z^{-1}-z} \,.\, [v = \exp(-2K_{\text{inv}})]. \quad . \quad . \quad (196)$$

It was this quantity which entered similarly for the spontaneous magnetization of the three lattices. The reduction is achieved by the use of the Landen transformation (Bateman Manuscript project, 1953, p. 319)

$$\mathscr{K}[2/(\kappa_1^{1/2}+\kappa_1^{-1/2})] = (1+\kappa_1)\mathscr{K}(\kappa_1) \quad (\kappa_1 \leqslant 1). \quad . \quad . \quad (197)$$

For the quadratic lattice relation (43) enables us to express functions of K, in terms of κ_1. We have

$$\frac{1}{\sinh 2K} = \frac{1}{(\sinh 2K)^{1/2}(\sinh 2K)^{1/2}} = \left(\frac{\sinh 2K_{\text{inv}}}{\sinh 2K}\right)^{1/2} = \kappa_1^{1/2}. \quad (198)$$

Applying this to (177) we find that

$$\xi_1 = \kappa_1^{1/2} + \kappa_1^{-1/2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (199)$$

and hence using (191) and (197)

$$E/J = -\coth 2K\left[1 + \frac{2}{\pi}(1-\kappa_1)\mathscr{K}(\kappa_1)\right]. \quad . \quad . \quad . \quad (200)$$

When $\kappa_1 \geqslant 1$, it is clear from (197) that κ_1^{-1} must replace κ_1 in the right-hand side; hence in (200) $\mathscr{K}(\kappa_1)$ should be replaced by $\kappa_1^{-1}\mathscr{K}(\kappa_1^{-1})$.

Analogous results may be obtained for the triangular and honeycomb lattices although the details are more involved. For the triangular lattice we use the relation (58) and define

$$g_1 = (v^{-2}-1)/(z^{-2}-1). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (201)$$

In the same manner as (198) all quantities can be expressed in terms of g_1, and it can be shown that the modulus of the elliptic integral in (182) is $2/(\kappa_1^{1/2}+\kappa_1^{-1/2})$. Using (197) we find that

$$I_2(\eta_1)=\frac{2}{\pi}\frac{g_1}{\sqrt{(1+2g_1)}}\mathscr{K}(\kappa_1) \quad (\kappa_1\leqslant 1) \quad . \quad . \quad . \quad (202)$$

with $\mathscr{K}(\kappa_1)$ being replaced by $\kappa_1^{-1}\mathscr{K}(\kappa_1^{-1})$ for $\kappa_1\geqslant 1$. For the honeycomb lattice the relation (202) is valid, but g_1 is defined by analogy with (61):

$$g_1=(\cosh 2K_{\text{inv}}-1)/(\cosh 2K-1). \quad . \quad . \quad . \quad (203)$$

For both of these lattices κ_1 is defined as for the quadratic lattice,

$$\kappa_1=\sinh 2K_{\text{inv}}/\sinh 2K.$$

The results (200), (202) can be combined into the following formulae which are similar to those given by Houtappel (1950) for the three lattices:

$$\left.\begin{aligned} E/J&=-\coth 2K+\frac{2}{\pi}\epsilon_1(K)\mathscr{K}(\kappa),\\ C_{\text{v}}/k&=K^2\left[-2/(\sinh 2K)^2+\frac{2}{\pi}\left(\frac{d\epsilon_1}{dK}-\frac{\epsilon_1}{\kappa}\frac{d\kappa}{dK}\right)\right.\\ &\qquad\left.+\frac{2\epsilon_1}{\pi(1-\kappa^2)\kappa}\frac{d\kappa}{dK}\right]. \end{aligned}\right\} \quad (204)$$

For C_{v} we have again used the relation (193). The values of $\epsilon_1(K)$ and κ are given in table 2, and various other properties of the lattices are summarized. The variable g_1 has been retained so as to demonstrate the symmetry of the inversion transformation. For $T>T_{\text{c}}$, z and v can be interchanged, and g_1 becomes g_1^{-1}; thus values of the energy and specific heat in the region above the Curie point can be obtained with little additional calculation from the values below the Curie point. Near the Curie point the specific heat is given approximately by (128) and (132).

The spontaneous magnetization per spin of the quadratic triangular and honeycomb lattices is given by the formula

$$I/m=(1-\kappa_1^2)^{1/8} \quad (T\leqslant T_{\text{c}}). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (205)$$

For the kagomé lattice it is (Naya 1954)

$$I/m=\frac{(1+3z^2)^{1/2}(1-z^2)^{1/2}}{(1+z^2)}\left[1-\frac{128z^6(1+z^2)^3(1+3z^4)}{(1-z^2)^6(1+3z^2)^2}\right]^{1/8} \quad . \quad . \quad (206)$$

1.5. *Antiferromagnetic Calculations*

To derive the solution for antiferromagnetism we replace K by $-K$ in all the formulae. For the quadratic and honeycomb lattices these formulae remain unchanged. For the triangular and kagomé lattices however C_1 and D_1 change in a fundamental manner. There is now no value of K at which the integral in (176) becomes zero; there is therefore no singularity and the thermodynamic functions behave smoothly and analytically. However as $K\to\infty$ (i.e. $T\to 0$) C_1 and D_1 are of the same order

Table 2. Parameters for Calculation of Thermodynamic Properties of Quadratic, Triangular, and Honeycomb Lattices

Lattice	Inversion transformation	g_1	κ	ϵ_1†
Quadratic	$(z^{-1}-z)(v^{-1}-v)=4$	$g_Q=2/(z^{-1}-z)$	$T<T_c,\ \kappa_Q=(v^{-1}-v)/(z^{-1}-z)$	$(1-g_Q^2)(1+g_Q^2)^{1/2}$
			$T>T_c,\ \kappa_Q^{-1}$	$(1-g_Q^2)g_Q^{-2}(1+g_Q^2)^{1/2}$
Triangular $(J>0)$	$(z^{-2}-1)(v^{-2}-1)=4$	$g_T=2/(z^{-2}-1)$	$T<T_c,\ \kappa_T=(v^{-1}-v)/z^{-1}-z)$	$(1-g_T^2)(g_T+2)(1+2g_T)^{-1/2}$
			$T>T_c,\ \kappa_T^{-1}$	$(1-g_T^2)g_T^{-3/2}(g_T+2)^{1/2}$
Honeycomb	$(z^{-1}-2+z)(v^{-1}-2+v)=4$	$g_H=2/(z^{-1}-2+z)$	$T<T_c,\ \kappa_H=(v^{-1}-v)/z^{-1}-z)$	$2(1-g_H^2)$
			$T>T_c,\ \kappa_H^{-1}$	$2(1-g_H^2)(1+2g_H)^{1/2}g_H^{-3/2}(g_H+2)^{-1/2}$
Triangular $(J<0)$			$\dfrac{(1+3z^2)^{1/2}(1-z^2)^{3/2}}{(1-3z^2)^{1/2}(1+z^2)^{3/2}}$	$\dfrac{2(3z^2-1)^{1/2}}{(z^2+1)^{1/2}(z^2-1)}$

† Note: $\kappa_Q=g_Q^2$, $\kappa_T^2=\dfrac{g_T(g_T+2)}{g_T^{-1}(g_T^{-1}+2)}$, $\kappa_H^2=\dfrac{g_H(g_H+2)}{g_H^{-1}(g_H^{-1}+2)}$

of magnitude; when we take out the terms corresponding to the lowest energy state [using the relation $k \ln \lambda_0 = S_0 - E_0/T$] we are left with an integral which represents a finite entropy. Hence the zero point entropies are given by:

(Triangular, Wannier 1950)

$$S_0/k = \frac{1}{8\pi^2}\int_0^{2\pi}\int_0^{2\pi} \ln\{3+2[\cos\theta+\cos\phi+\cos(\theta+\phi)]\}\,d\theta\,d\phi = 0{\cdot}32306,$$

(Kagomé, Kano and Naya 1953)

$$S_0/k = \frac{1}{24\pi^2}\int_0^{2\pi}\int_0^{2\pi} \ln\{21-4[\cos\theta+\cos\phi+\cos(\theta+\phi)]\,d\theta\,d\phi = 0{\cdot}50183. \qquad (207)$$

In regard to the thermodynamic functions, for the kagomé lattice η_1 is always positive, and (182), (184) are still valid. However, for the triangular lattice η_1 becomes negative, and an alternative reduction to standard form for a pair of conjugate complex roots is required instead of (180). The simplest method of deriving the solution for this case is to continue the ferromagnetic solution (202) for $T > T_c$ using the appropriate transformation of the elliptic integral†. Thus v given by (60) becomes negative when $J < 0$ and hence so does $\kappa_1{}^2$; we therefore use the transformation (Bateman Manuscript Project 1953, p. 319)

$$\mathscr{K}(ik_1/k_1') = k_1'\,\mathscr{K}(k_1), \qquad (208)$$

which in our case gives

$$\mathscr{K}(i\kappa_T{}^{-1}) = -\frac{\kappa_T{}^2}{1-\kappa_T{}^2}\,\mathscr{K}[1/(1-\kappa_T{}^2)^{1/2}]. \qquad (209)$$

The general formula (204) remains valid, with $\kappa(K)$ and $\epsilon_1(K)$ as given in table 2.

1.6. *Asymmetric Quadratic Net*

When the interactions differ in different directions in the lattice the reduction of the integrals to standard form is much more involved. Onsager (1944) carried out this reduction for the quadratic lattice, and we quote his results at the Curie point: $(\sinh 2K \sinh 2K' = 1)$,

$$E_c = -(2/\pi)(J' \operatorname{gd} 2K' \coth 2K' + J \operatorname{gd} 2K \coth 2K), \qquad (210)$$

$$\left.\begin{aligned} -F_c/kT &= \ln\lambda_c = \tfrac{1}{2}\ln 2 + (\tfrac{1}{2} - 2y_1)\ln\cot\pi y_1 + 2\int_0^{y_1}\ln\cot\pi x\,dx. \\ &(\pi y_1 = \operatorname{gd} 2K' = \tfrac{1}{2}\pi - \operatorname{gd} 2K). \end{aligned}\right\} \qquad (211)$$

Near the Curie point,

$$\left.\begin{aligned} C_V/k &\simeq (4/\pi)[K_2(K + K'\sinh 2K)^2 \sinh 2K' - K^2\sinh^2 2K' \operatorname{gd} 2K \\ &\quad - 2KK' - K'^2 \sinh^2 2K \operatorname{gd} 2K']. \\ K_2 &\simeq \tfrac{1}{2}[\ln(4T/|T-T_c|) - \ln(K\coth 2K + K'\coth 2K')]. \end{aligned}\right\} \qquad (212)$$

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† I am indebted to Dr. M. E. Fisher for this suggestion; he and Dr. M. F. Sykes have pointed out that there is a misprint in Houtappel's formula for $\epsilon_1(k)$ in the case $J < 0$, and that Wannier's transformation of the elliptic integral is in error.

Notation for § 3

χ_m magnetic susceptibility of chain of m units.

σ_x, σ_y, σ_z Pauli spin matrices.

$\langle\alpha_1\rangle$ $\langle\alpha_2\rangle$ mean fractions of spins pointing in directions 1 and 2 respectively.

$\langle\alpha_{11}{}^{ab}\rangle$ $\langle\alpha_{12}{}^{ab}\rangle$ $\langle\alpha_{21}{}^{ab}\rangle$ $\langle\alpha_{22}{}^{ab}\rangle$ mean fractions of pairs of spins of various types on sites a, b.

$\mathscr{S}_{ab}$ order parameter for sites, a, b. R long-range order ($\mathscr{S}_\infty = R^2$).

σ_i variable for spin at lattice point i taking values ∓ 1 according as spin i points in direction 1 or 2.

$K = J/kT$, $L = mH/kT$.

$\mathscr{N}$ number of nearest neighbour links of lattice.

Rectangular lattice. Interactions J, J'. Dimensions n horizontal m vertical ($N = mn$). Nearest neighbour links $\mathfrak{n}$ horizontal $\mathfrak{m}$ vertical.

$p(r)$ number of closed polygons which can be constructed with r nearest neighbour links of the quadratic lattice.

$p(r, s)$ number with r horizontal s veritcal links for rectangular lattice.

v = variable for inversion transformation, $z \to v$;

v_c, z_c critical values.

$\nu(r)$ number of low temperature configurations with r broken links.

* refers to dual lattice, e.g. K^*, N^*, $\mathscr{N}^*$.

$^+$ refers to star-triangle transformation, e.g. z^+, K^+.

$^-$ refers to decoration transformation, e.g. $\bar{K}$, $\bar{L}$.

Matrices $\mathbf{C}_i$, $\mathbf{s}_i$ are defined by

$$\mathbf{C}_i|\sigma_1 \ldots, \sigma_i, \ldots \sigma_n\rangle = |\sigma_1 \ldots, -\sigma_i, \ldots \sigma_n\rangle$$

$$\mathbf{s}_i|\sigma_1 \ldots, \sigma_i, \ldots \sigma_n\rangle = \sigma_i|\sigma_1 \ldots, \sigma_i, \ldots \sigma_n\rangle$$

Quantities related to exact solution of two-dimensional Ising model ($H = 0$)

$\lambda_1 \ldots \lambda_r \ldots$ eigenvalues of matrix $\mathbf{V}$. $\lambda(z)$ partition function.

$\gamma_1, \ldots \gamma_{2n}$ defined by (92) in terms of which λ_i can be simply expressed.

λ_b, λ_b', partition functions for boundaries; σ, σ' boundary tensions.

$F_r(N, z)$ defined by (140), $f_r(z)$ by (143), $g_r(z)$ by (146).

$y = z^{-1}$, $\Lambda^{(a)}(\mu, y)$ used in formulae for an antiferromagnetic.

$\tau = (1-\mu)/(1+\mu)$, $\Phi_r(\mathscr{N}, \tau)$ defined by (155), $\phi_r(\tau)$ by (157),

$\theta(z) = \underset{\mu \to 1}{\mathrm{Lt}} (\mu\Lambda_\mu/\Lambda)$, $\delta(z) = \underset{\mu \to 1}{\mathrm{Lt}} (\mu^2\Lambda_{\mu\mu}/\Lambda)$.

η_1, η_2 fractions of spins in sub-lattices 2, 1 which have overturned.

α_c critical concentration in a superlattice below which long-range order disappears.

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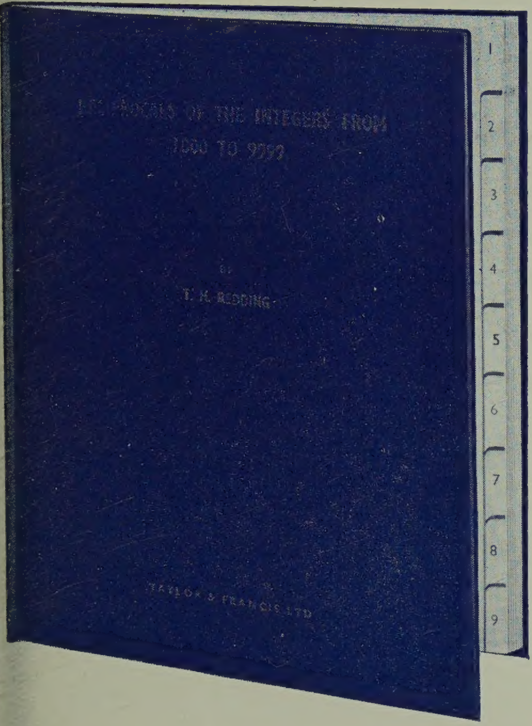
[To be concluded in Vol. 9, No. 35, July 1960]

FOR USERS OF CALCULATORS



RECIPROCALS OF THE INTEGERS FROM 1000 TO 9999

By T. H. Redding
M.Sc.(Lond.), A.M.I.Mech.E., A.F.R.Ae.S.

Arranged for use with mechanical calculating machines to facilitate the evaluation of quotients and compound fractions

With an Appendix on mechanical barrel-setting calculators

These tables list the 10^6 multiples of the reciprocals of the integers 1000 to 9999 and are displayed as 1000 entries on each of nine double-page spreads which are thumb-indexed (1000 . . . , 2000 . . . , 3000 . . . , . . . etc) to facilitate rapid manipulation with one hand only. The entries are direct reading and are correct to the nearest integer in the third place of decimals.

Although suitable for general use, the tables have been prepared and arranged in a manner particularly suitable for use in conjunction with mechanical computing machines of the " barrel-setting " type in the evaluation of quotients and compound fractions. Equally the tables find application in effecting the evaluation of quotients on adding and listing machines when these incorporate a mechanism for automatically evaluating simple products.

In the first instance it was anticipated that an Appendix dealing with the advantages to be gained by the use of the reciprocal function in conjunction with such machines—and particularly with barrel-setting machines—would suffice to ensure the best use being made of the tables. The present 22-page *Appendix*, however, goes further than this, since the discussion of the tables is prefaced by a description of barrel-setting machines and their (simplest) method of operation in the evaluation of products, quotients and compound fractions. Thus, the description of each calculating procedure is followed by a numerical example with accompanying diagrams to illustrate the keyboard-displays at the beginning, the end, and at intermediate stages in the calculation. The machine-evaluation of series comprising the sum of a number of product or quotient-terms is also discussed. Generally it is hoped that the Appendix will serve as an introduction to mechanical methods of computation and that it will materially assist prospective purchasers in the choice of a machine.

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